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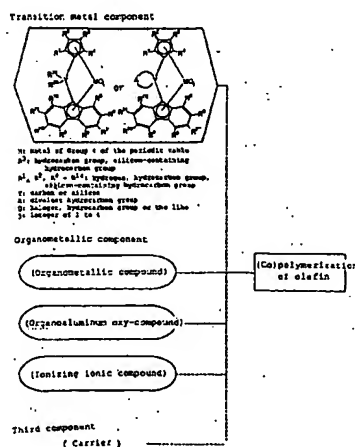
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(54) METALLOCENE COMPOUND, PROCESS FOR PRODUCING METALLOCENE COMPOUND, OLEFIN POLYMERIZATION CATALYST, PROCESS FOR PRODUCING POLYOLEFIN, AND POLYOLEFIN

(57) The metallocene compound according to the invention and the olefin polymerization catalyst containing the compound are intended to produce a catalyst capable of preparing an isotactic polymer with a high polymerization activity. The metallocene compound contains a substituted cyclopentadienyl group and a (substituted) fluorenyl group and has a structure where in these groups are bridged by a hydrocarbon group or the like. The process for preparing a metallocene compound according to the invention is intended to selectively prepare a specific metallocene compound so as not to produce an isomer, and in this process an intermediate product is synthesized by a specific method. The process for preparing a polyolefin according to the invention is intended to prepare a polyolefin having excellent impact resistance and transparency, and this process comprises homopolymerizing an  $\alpha$ -olefin of 3 to 8 carbon atoms or copolymerizing an olefin of 3 to 8 carbon atoms and another  $\alpha$ -olefin in the presence of

an olefin polymerization catalyst containing the above-mentioned metallocene compound.

Fig. 1



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## Description

## TECHNICAL FIELD

5 [0001] The present invention relates to a metallocene compound having a specific structure, a process for preparing the metallocene compound, an olefin polymerization catalyst containing the metallocene compound, a process for preparing a polyolefin using the olefin polymerization catalyst, and a polyolefin.

## BACKGROUND ART

10 [0002] The "metallocene compound" is well known as a homogeneous catalyst for olefin polymerization. Since the isotactic polymerization was reported by W. Kaminsky, et al. (Angew. Chem. Int. Ed. Engl., 24, 507 (1985)), there have been made many improvements in the olefin polymerization process using a metallocene compound, particularly a process for stereoregularly polymerizing an  $\alpha$ -olefin. As an example of the improvement, a metallocene compound  
 15 having a C2 symmetric structure wherein some hydrogen atoms of the cyclopentadienyl group in the ligand part are replaced with alkyl groups has been reported (by Yamazaki, et al., Chemistry Letters, 1853 (1989), Japanese Patent Laid-Open Publication No. 268307/1992). As like attempts, further, a large number of attempts to improve the isotactic stereoregularity of an olefin polymer by the use of a metallocene compound having, as a ligand, a bisindenyl derivative having a C2 symmetric structure have been reported (e.g., Angew. Chem. Int. Ed. Engl., 31, 1347 (1992), Organometallics, 13, 954 (1994)).

20 [0003] The metallocene compound of the C2 symmetric structure, however, is usually obtained as a mixture of a racemic modification and a mesoisomer, and only the racemic modification provides an isotactic polymer, while obtainable from the mesoisomer is only an atactic polymer, so that it is necessary to separate the racemic modification and the mesoisomer from each other in order to selectively obtain the isotactic polymer.

25 [0004] On the other hand, J.A. Ewen has found that an  $\alpha$ -olefin is polymerized with syndiotactic stereoregularity by the use of a metallocene compound having a Cs symmetric structure wherein the cyclopentadienyl group and the fluorenyl group are bridged by dimethylmethylene (J. Am. Chem. Soc., 110, 6255 (1988)). To improve the metallocene compound, an attempt to introduce tert-butyl groups at the 2-position and the 7-position of the fluorenyl group and thereby further control the syndiotactic stereoregularity has been made (Japanese Patent Laid-Open Publication No.  
 30 69394/1992).

[0005] In addition, an attempt to synthesize an isotactic polymer by the use of a metallocene compound having a C1 symmetric structure that is different from the C2 symmetric and the Cs symmetric structures has been reported (see, for example, Japanese Patent Laid-Open Publications No. 193796/1991 and No. 122718/1994, EP 0881236).

35 [0006] The polymerization activities of these metallocene compounds, however, are still insufficient, and hence development of metallocene compounds having excellent polymerization activities and olefin polymerization catalysts containing such metallocene compounds has been desired.

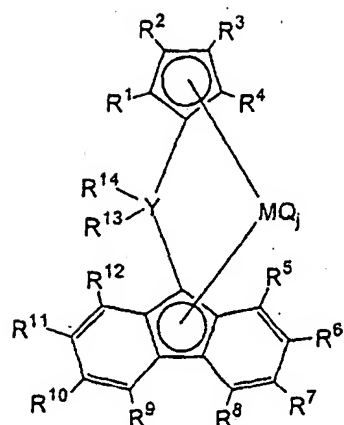
[0007] The metallocene compounds having Cs and C1 symmetric structures have an advantage in that the structural isomers such as a mesoisomer and a racemic modification are not produced, differently from the metallocene compound having a C2 symmetric structure.

40 [0008] Of the above metallocene compounds, the metallocene compound of the C1 symmetric structure, however, has a problem in that an unnecessary isomer wherein the substituent group is attached at a position different from the intended proper position is produced depending upon the preparation process. When such an isomer is used as, for example, an olefin polymerization catalyst, unfavorable results such as production of an atactic polymer as a by-product are often brought about. Hence, development of a process for selectively preparing a metallocene compound in which  
 45 such an unnecessary isomer is not included has been desired.

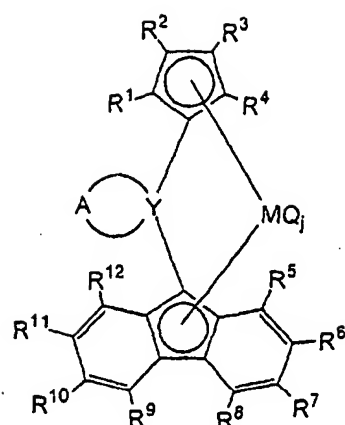
## DISCLOSURE OF THE INVENTION

50 [0009] The metallocene compound according to the invention is represented by the following formula (1) or (2):

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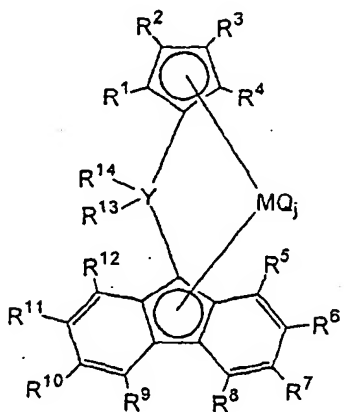
... (1)



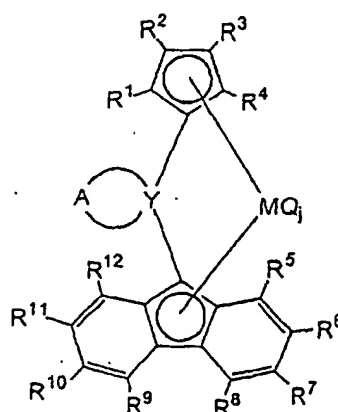
... (2)

wherein  $R^3$  is selected from a hydrocarbon group and a silicon-containing hydrocarbon group;  $R^1$ ,  $R^2$ ,  $R^4$ ,  $R^5$ ,  $R^6$ ,  $R^7$ ,  $R^8$ ,  $R^9$ ,  $R^{10}$ ,  $R^{11}$ ,  $R^{12}$ ,  $R^{13}$  and  $R^{14}$  may be the same or different and are each selected from a hydrogen atom, a hydrocarbon group and a silicon-containing hydrocarbon group; of the groups indicated by  $R^1$  to  $R^{12}$ , neighboring groups may be bonded to form a ring; in case of the formula (1), a group selected from  $R^1$ ,  $R^4$ ,  $R^5$  and  $R^{12}$  may be bonded to  $R^{13}$  or  $R^{14}$  to form a ring; A is a divalent hydrocarbon group of 2 to 20 carbon atoms which may contain an unsaturated bond and/or an aromatic ring; A may contain two or more cyclic structures including a ring formed by A in cooperation with Y; Y is a carbon atom or a silicon atom; M is a metal selected from Group 4 of the periodic table; j is an integer of 1 to 4; Q is selected from a halogen atom, a hydrocarbon group, an anionic ligand and a neutral ligand capable of coordination by a lone pair; and when j is 2 or greater, each Q may be the same or different.

[0010] Another embodiment of the metallocene compound of the invention is represented by the following formula (1a) or (2a):



(1a)

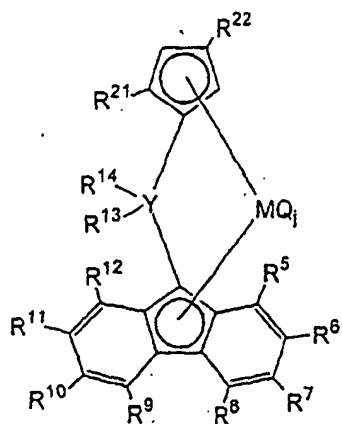


(2a)

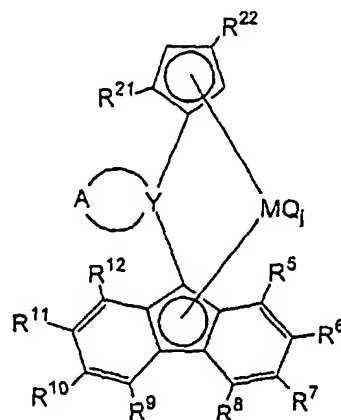
wherein  $R^3$  is selected from a hydrocarbon group and a silicon-containing hydrocarbon group;  $R^1$ ,  $R^2$ ,  $R^4$ ,  $R^5$ ,  $R^6$ ,  $R^7$ ,  $R^8$ ,  $R^9$ ,  $R^{10}$ ,  $R^{11}$ ,  $R^{12}$ ,  $R^{13}$  and  $R^{14}$  may be the same or different and are each selected from a hydrogen atom, a hydrocarbon group and a silicon-containing hydrocarbon group; in case of a compound of the formula (1a), when  $R^3$  is a tert-butyl group or a trimethylsilyl group and when  $R^{13}$  and  $R^{14}$  are methyl groups or phenyl groups at the same

time,  $R^6$  and  $R^{11}$  are not hydrogen atoms at the same time; of the groups indicated by  $R^1$  to  $R^{12}$ , neighboring groups may be bonded to form a ring; in case of the formula (1a), a group selected from  $R^1$ ,  $R^4$ ,  $R^5$  and  $R^{12}$  may be bonded to  $R^{13}$  or  $R^{14}$  to form a ring; A is a divalent hydrocarbon group of 2 to 20 carbon atoms which may contain an unsaturated bond and/or an aromatic ring; A may contain two or more cyclic structures including a ring formed by A in cooperation with Y; Y is a carbon atom or a silicon atom; M is a metal selected from Group 4 of the periodic table; j is an integer of 1 to 4; Q is selected from a halogen atom, a hydrocarbon group; an anionic ligand and a neutral ligand capable of coordination by a lone pair; and when j is 2 or greater, each Q may be the same or different.

[0011] A further embodiment of the metallocene compound of the invention is represented by the following formula (1b) or (2b):



... (1b)



... (2b)

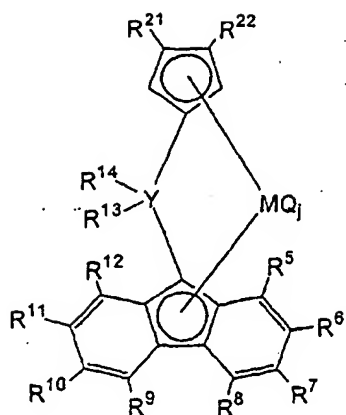
wherein  $R^{21}$  and  $R^{22}$  may be the same or different and are each selected from a hydrocarbon group and a silicon-containing hydrocarbon group;  $R^5$ ,  $R^6$ ,  $R^7$ ,  $R^8$ ,  $R^9$ ,  $R^{10}$ ,  $R^{11}$ ,  $R^{12}$ ,  $R^{13}$  and  $R^{14}$  may be the same or different and are each selected from a hydrogen atom, a hydrocarbon group and a silicon-containing hydrocarbon group; of the groups indicated by  $R^5$  to  $R^{12}$ , neighboring groups may be bonded to form a ring; A is a divalent hydrocarbon group of 2 to 20 carbon atoms which may contain an unsaturated bond and/or an aromatic ring; A may contain two or more cyclic structures including a ring formed by A in cooperation with Y; M is a metal selected from Group 4 of the periodic table; Y is a carbon atom or a silicon atom; j is an integer of 1 to 4; Q is selected from a halogen atom, a hydrocarbon group, an anionic ligand and a neutral ligand capable of coordination by a lone pair; and when j is 2 or greater, each Q may be the same or different.

[0012] The process for preparing a metallocene compound according to the invention comprises selectively preparing a metallocene compound represented by the above formula (1b) or (2b) so as not to include an isomeric compound represented by the following formula (3b), (4b), (5b) or (6b):

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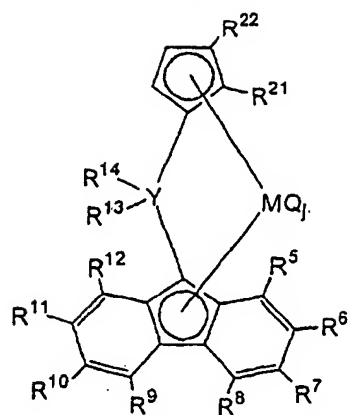
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... (3b)

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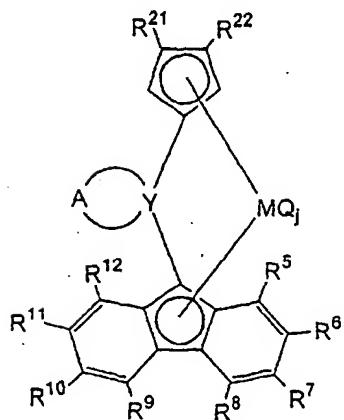


... (4b)

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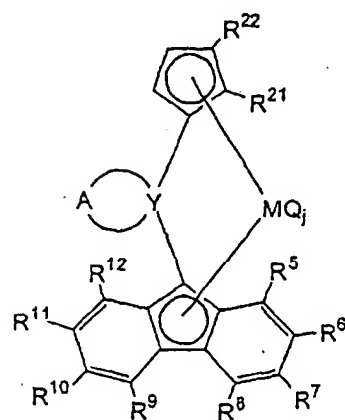
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... (5b)

40



... (6b)

wherein  $R^{21}$ ,  $R^{22}$ ,  $R^5$  to  $R^{14}$ , A, M, Y, Q and j have the same meanings as those of  $R^{21}$ ,  $R^{22}$ ,  $R^5$  to  $R^{14}$ , A, M, Y, Q and j in the formula (1b) or (2b), respectively.

[0013] In the present invention, it is preferable that a ligand precursor represented by the following formula (7b) or (8b) is selectively prepared so as not to include an isomeric compound represented by the following formula (9b), (10b), (11b) or (12b) and the resulting ligand precursor is used as a material to selectively prepare the metallocene compound represented by the formula (1b) or (2b);

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by adding hydrogen in amount of about 0.01 to 100 NL based on 1 kg of the olefin.

[0197] In the present invention, as olefins used in the polymerization reaction preferable are those of 2 to 20 carbon atoms, particularly  $\alpha$ -olefins of 2 to 10 carbon atoms. Example of the olefins include ethylene, propylene, 1-butene, 1-pentene, 1-hexene, 3-methyl-1-butene, 3-methyl-1-pentene, 3-ethyl-1-pentene, 4-methyl-1-pentene, 4-methyl-1-hexene, 4,4-dimethyl-1-hexene, 4,4-dimethyl-1-pentene, 4-ethyl-1-hexene, 3-ethyl-1-hexene, 1-octene, 1-decene, 1-dodecene, 1-tetradecene, 1-hexadecene, 1-octadecene, 1-eicosene, vinylcyclohexane and styrene.

[0198] Further examples include dienes of 4 to 20 carbon atoms such as butadiene, 1,4-pentadiene, 1,5-hexadiene and 1,4-hexadiene, cycloolefins such as dicyclopentadiene, norbornene, methylnorbornene, tetracyclododecene and methyltetracyclododecene and silicon-containing olefins such as allyltrimethylsilane and vinyltrimethylsilane.

[0199] Of the olefin polymerization catalysts according to the invention, the catalyst containing the metallocene compound represented by the formula (1) or (2) is favorably used for copolymerization of at least 2 kinds of olefins.

[0200] At least one of the olefins used is preferably an  $\alpha$ -olefin of 4 or less carbon atoms.

[0201] The copolymerization of two or more olefins using the olefin polymerization catalyst of the invention has advantages such as high polymerization activity and good copolymerizability and is characterized in that a copolymer of desired properties can be obtained.

[0202] An example of the copolymer obtained from two or more olefins is a copolymer comprising recurring units ( $U_1$ ) derived from one  $\alpha$ -olefin selected from  $\alpha$ -olefins of 3 to 8 carbon atoms in amounts of 50 to 99.9 % by mol and recurring units ( $U_2$ ) other than the recurring units ( $U_1$ ), said recurring units ( $U_2$ ) being derived from at least one  $\alpha$ -olefin selected from  $\alpha$ -olefins of 2 to 20 carbon atoms, in amounts of 50 to 0.1 % by mol.

[0203] Examples of the  $\alpha$ -olefins of 3 to 8 carbon atoms include propylene, 1-butene, 1-pentene, 1-hexene, 3-methyl-1-butene, 3-methyl-1-pentene, 3-ethyl-1-pentene, 4-methyl-1-pentene, 4-methyl-1-hexene, 4,4-dimethyl-1-hexene, 4,4-dimethyl-1-pentene, 4-ethyl-1-hexene, 3-ethyl-1-hexene and 1-octene. Examples of the  $\alpha$ -olefins of 2 to 20 carbon atoms include the same ones as described above.

[0204] Such a copolymer is, for example, a copolymer comprising propylene units in amounts of 50 to 99.5 % by mol and units of an  $\alpha$ -olefin of 2 to 20 carbon atoms other than propylene in amounts of 50 to 0.5 % by mol.

[0205] The random copolymer comprising propylene units in amounts of 95 to 99.5 % by mol and units of an  $\alpha$ -olefin of 2 to 20 carbon atoms other than propylene in amounts of 5 to 0.5 % by mol preferably has the following properties: the pentad isotacticity as determined from  $^{13}\text{C}$ -NMR spectrum measurement is not less than 80 %, preferably not less than 85 %; the proportion of 2,1-insertion and the proportion of 1,3-insertion are each not more than 0.2 %, preferably not more than 0.1 %; the MFR is in the range of 0.01 to 1000 g/10 min, preferably 0.01 to 500 g/10 min; the molecular weight distribution ( $M_w/M_n$ ) as calculated from molecular weights ( $M_w$ : weight-average molecular weight,  $M_n$ : number-average molecular weight) measured by gel permeation chromatography (GPC) is in the range of 1 to 3, preferably 1 to 2.5, more preferably 1 to 2.3; and the quantity of a decane-soluble component (after the polymer is treated with n-decane at 150°C for 2 hours and cooled to room temperature, the amount (weight %) of the polymer dissolved in the n-decane is measured) is not more than 2 % by weight, preferably not more than 1 % by weight.

[0206] Of the olefin polymerization catalysts according to the invention, the catalyst containing the metallocene compound represented by the formula (1a) or (2a) is favorably used for homopolymerization of an olefin.

[0207] The homopolymerization of an  $\alpha$ -olefin of 3 or more carbon atoms using the olefin polymerization catalyst of the invention is characterized in that an olefin polymer having high stereoregularity can be obtained and the polymer usually has high isotacticity.

[0208] The homopolymer of an  $\alpha$ -olefin of 3 or more carbon atoms, particularly polypropylene, preferably has the following properties: the pentad isotacticity as determined from  $^{13}\text{C}$ -NMR spectrum measurement is not less than 85 %, preferably not less than 90 %, more preferably not less than 95 %; the proportion of 2,1-insertion and the proportion of 1,3-insertion are each not more than 0.2 %, preferably not more than 0.1 %, more preferably not more than 0.05 %; the melting point ( $T_m$ ) as measured by differential scanning calorimetry (DSC) is not lower than 140°C, preferably not lower than 150°C, more preferably not lower than 153°C; the MFR is in the range of 0.01 to 1000 g/10 min, preferably 0.01 to 500 g/10 min; the molecular weight distribution ( $M_w/M_n$ ) as calculated from molecular weights measured by GPC is in the range of 1 to 3, preferably 1 to 2.5, more preferably 1 to 2.3; and the quantity of a decane-soluble component is not more than 2 % by weight, preferably not more than 1 % by weight, more preferably not more than 0.5 % by weight.

[0209] Of the olefin polymerization catalysts according to the invention, the catalyst containing the metallocene compound represented by the formula (1b) or (2b) is favorably used for homopolymerization of an olefin or copolymerization of at least two kinds of olefins.

[0210] Of the polymers obtained by the use of such a catalyst, a homopolymer of an  $\alpha$ -olefin of 3 to 8 carbon atoms, particularly polypropylene, preferably has the following properties: the pentad isotacticity as determined from  $^{13}\text{C}$ -NMR spectrum measurement is not less than 85 %, preferably not less than 90 %, more preferably not less than 95 %; the proportion of 2,1-insertion and the proportion of 1,3-insertion are each not more than 0.2 %, preferably not more than 0.1 %, more preferably not more than 0.05 %; the melting point ( $T_m$ ) as measured by DSC is not lower than 140°C,

preferably not lower than 150°C, more preferably not lower than 153°C; the MFR is in the range of 0.01 to 1000 g/10 min; preferably 0.01 to 500 g/10 min; the molecular weight distribution (Mw/Mn) as calculated from molecular weights measured by GPC is in the range of 1 to 3, preferably 1 to 2.5, more preferably 1 to 2.3; and the quantity of a decane-soluble component is not more than 2 % by weight, preferably not more than 1 % by weight, more preferably not more than 0.5 % by weight.

[0211] An example of the copolymer obtained from two or more olefins using the catalyst containing the metallocene compound represented by the formula (1b) or (2b) is a copolymer comprising recurring units ( $U_1$ ) derived from one  $\alpha$ -olefin selected from  $\alpha$ -olefins of 3 to 8 carbon atoms in amounts of 50 to 99.9 % by mol and recurring units ( $U_2$ ) other than the recurring units ( $U_1$ ), said recurring units ( $U_2$ ) being derived from at least one  $\alpha$ -olefin selected from  $\alpha$ -olefins of 2 to 20 carbon atoms, in amounts of 50 to 0.1 % by mol.

[0212] Such a copolymer is, for example, a copolymer comprising propylene units in amounts of 50 to 99.5 % by mol and units of an  $\alpha$ -olefin other than propylene in amounts of 50 to 0.5 % by mol.

[0213] The copolymer comprising propylene units in amounts of 95 to 99.5 % by mol and units of an  $\alpha$ -olefin of 2 to 20 carbon atoms other than propylene in amounts of 5 to 0.5 % by mol preferably has the following properties: the pentad isotacticity as determined from  $^{13}\text{C}$ -NMR spectrum measurement is not less than 80 %, preferably not less than 85 %; the proportion of 2,1-insertion and the proportion of 1,3-insertion are each not more than 0.2 %, preferably not more than 0.1 %; the MFR is in the range of 0.01 to 1000 g/10 min, preferably 0.01 to 500 g/10 min; the molecular weight distribution (Mw/Mn) as calculated from molecular weights measured by GPC is in the range of 1 to 3, preferably 1 to 2.5, more preferably 1 to 2.3; and the quantity of a decane-soluble component is not more than 2 % by weight, preferably not more than 1 % by weight.

#### Polyolefin

[0214] The polyolefin according to the invention is a polyolefin comprising recurring units ( $U_1$ ) derived from one  $\alpha$ -olefin selected from  $\alpha$ -olefins of 3 to 8 carbon atoms in amounts of 50 to 100 % by mol, preferably 65 to 100 % by mol, more preferably 80 to 100 % by mol, and recurring units ( $U_2$ ) other than the recurring units ( $U_1$ ), said recurring units ( $U_2$ ) being derived from at least one olefin selected from  $\alpha$ -olefins of 2 to 20 carbon atoms, in amounts of 50 to 0 % by mol, preferably 35 to 0 % by mol, more preferably 20 to 0 % by mol.

[0215] Examples of the  $\alpha$ -olefins of 3 to 8 carbon atoms and the  $\alpha$ -olefins of 2 to 20 carbon atoms include the same ones as previously described.

[0216] This polyolefin satisfies the following requisites (i) to (iii):

(i) the proportion of 2,1-insertion and the proportion of 1,3-insertion are each not more than 0.2 %, preferably not more than 0.1 %,

(ii) the molecular weight distribution (Mw/Mn) as determined by (GPC) is in the range of 1 to 3, preferably 1 to 2.5, more preferably 1 to 2.3, and

(iii) the quantity of a decane-soluble component is not more than 2 % by weight, preferably not more than 1 % by weight.

[0217] The polyolefin preferably comprises recurring units derived from propylene in amounts of 50 to 99.5 % by mol, preferably 65 to 99.5 % by mol, more preferably 80 to 99.5 % by mol, and recurring units derived from at least one olefin selected from  $\alpha$ -olefins of 2 to 20 carbon atoms other than propylene in amounts of 50 to 0.5 % by mol, preferably 35 to 0.5 % by mol, more preferably 20 to 0.5 % by mol.

[0218] Such a polyolefin of the invention has excellent elastic modulus, impact resistance and transparency.

[0219] Another embodiment of the polyolefin of the invention is a homopolymer of one  $\alpha$ -olefin selected from  $\alpha$ -olefins of 3 to 8 carbon atoms.

[0220] Examples of the  $\alpha$ -olefins of 3 to 8 carbon atoms include the same ones as previously described.

[0221] This polyolefin satisfies the following requisites (i) to (vi):

(i) the pentad isotacticity as determined from  $^{13}\text{C}$ -NMR spectrum measurement is not less than 85 %, preferably not less than 90 %, more preferably not less than 95 %,

(ii) the proportion of 2,1-insertion and the proportion of 1,3-insertion are each not more than 0.2 %, preferably not more than 0.1 %, more preferably not more than 0.05 %,

(iii) the MFR is in the range of 0.01 to 1000 g/10 min, preferably 0.01 to 500 g/10 min, more preferably 0.02 to 400 g/10 min,

(iv) the molecular weight distribution (Mw/Mn) as determined by GPC is in the range of 1 to 3, preferably 1 to 2.5, more preferably 1 to 2.3,

(v) the quantity of a decane-soluble component is not more than 2 % by weight, preferably not more than 1 % by

weight, more preferably not more than 0.5 % by weight, and

(vi) the melting point ( $T_m$ ) as measured by DSC is not lower than 140°C, preferably not lower than 150°C, more preferably not lower than 153°C.

[0222] The polyolefin is preferably a homopolymer of propylene.

[0223] Such a polyolefin of the invention has excellent elastic modulus, impact resistance and transparency.

[0224] A further embodiment of the polyolefin of the invention is a polyolefin comprising recurring units ( $U_1$ ) derived from one  $\alpha$ -olefin selected from  $\alpha$ -olefins of 3 to 8 carbon atoms in amounts of 95 to 99.5 % by mol, preferably 95 to 99 % by mol, more preferably 95 to 98 % by mol, and recurring units ( $U_2$ ) other than the recurring units ( $U_1$ ), said recurring units ( $U_2$ ) being derived from at least one olefin selected from  $\alpha$ -olefins of 2 to 20 carbon atoms, in amounts of 5 to 0.05 % by mol, preferably 5 to 1 % by mol, more preferably 5 to 2 % by mol.

[0225] Examples of the  $\alpha$ -olefins of 3 to 8 carbon atoms and the  $\alpha$ -olefins of 2 to 20 carbon atoms include the same ones as previously described.

[0226] This polyolefin satisfies the following requisites (i) to (vi):

(i) the pentad isotacticity as determined from  $^{13}\text{C}$ -NMR spectrum measurement is not less than 80 %, preferably not less than 85 %,

(ii) the proportion of 2,1-insertion and the proportion of 1,3-insertion are each not more than 0.2 %, preferably not more than 0.1 %,

(iii) the MFR is in the range of 0.01 to 1000 g/10 min, preferably 0.01 to 500 g/10 min, more preferably 0.02 to 400 g/10 min,

(iv) the molecular weight distribution ( $M_w/M_n$ ) as determined by GPC is in the range of 1 to 3, preferably 1 to 2.5, more preferably 1 to 2.3,

(v) the quantity of a decane-soluble component is not more than 2 % by weight, preferably not more than 1 % by weight, more preferably not more than 0.5 % by weight, and

(vi) the melting point ( $T_m$ ) as measured by a differential scanning calorimeter is not higher than 145°C, preferably not higher than 140°C.

[0227] The polyolefin preferably comprises recurring units derived from propylene in amounts of 95 to 99.5 % by mol, preferably 95 to 99 % by mol, more preferably 95 to 98 % by mol, and recurring units derived from at least one olefin selected from  $\alpha$ -olefins of 2 to 20 carbon atoms other than propylene in amounts of 5 to 0.5 % by mol, preferably 5 to 1 % by mol, more preferably 5 to 2 % by mol.

[0228] Such a polyolefin of the invention has excellent elastic modulus, impact resistance and transparency.

[0229] The polyolefin of the invention mentioned above can be prepared by polymerizing or copolymerizing the corresponding olefin under the above-mentioned conditions using the olefin polymerization catalyst containing the metallocene compound represented by the formula (1), (2), (1a), (2a), (1b) or (2b).

#### EFFECT OF THE INVENTION

[0230] The metallocene compound represented by the formula (1) or (2) according to the invention and the olefin polymerization catalyst containing this metallocene compound have excellent olefin polymerization activity and are of industrially great value. The olefin copolymer obtained by the use of the catalyst, particularly a propylene random copolymer, has excellent elastic modulus, impact resistance and transparency.

[0231] The metallocene compound represented by the formula (1a) or (2a) according to the invention and the olefin polymerization catalyst containing this metallocene compound have excellent olefin polymerization activity and are of industrially great value. The poly- $\alpha$ -olefin obtained by the use of the catalyst, particularly polypropylene, has excellent elastic modulus, impact resistance and transparency.

[0232] The metallocene compound represented by the formula (1b) or (2b) according to the invention and the olefin polymerization catalyst containing this metallocene compound have excellent olefin polymerization activity and are of industrially great value. The poly- $\alpha$ -olefin obtained by the use of the catalyst, particularly polypropylene, has excellent elastic modulus, impact resistance and transparency. The olefin copolymer obtained by the use of the catalyst, particularly a propylene random copolymer, has excellent elastic modulus, impact resistance and transparency.

[0233] The process for preparing a metallocene compound according to the invention is excellent as a process for selectively preparing a metallocene compound having a desirable specific structure, and is of industrially great value.

[0234] The polyolefin according to the invention has excellent elastic modulus, impact resistance and transparency.

[0235] The polyolefin according to the invention can be favorably used for nonwoven fabrics, films, sealants, industrial materials, transparent injection, block polymers, alloys, modifiers, etc., and can be broadly used specifically for hygienic materials, civil engineering materials, automobile parts, electrical appliances, food containers, packaging materials,



miscellaneous goods, etc.

# EXAMPLE

5 [0236] The present invention is further described with reference to the following examples, but it should be construed that the invention is in no way limited to those examples.

[0237] In the present invention, the melting point ( $T_m$ ) of a polymer was determined as follows. Through differential scanning calorimetry (DSC), a polymer sample kept at 240°C for 10 minutes was cooled to 30°C, kept for 5 minutes and then heated at a rate of 10°C/min to obtain a crystal melting peak, from which the melting point was calculated.

10 [0238] The molecular weight ( $M_w$ ,  $M_n$ ) was measured by GPC (gel permeation chromatography).

[0239] The quantity of a decane-soluble component was determined as follows. A polymer was treated with n-decene at 150°C for 2 hours and then cooled to room temperature, and the quantity of the polymer (% by weight) dissolved in n-decene was measured.

15 [0240] The stereoregularity (pentad isotacticity (mmmm), 2,1-insertion, 1,3-insertion) of a polymer was determined from  $^{13}\text{C}$ -NMR spectrum measurement.

[0241] The intrinsic viscosity ( $\eta$ ) was measured in decalin at 135°C.

[0242] The MFR was measured after heating of a polymer at 230°C for 6 minutes.

## Example 1

20

### Synthesis of dimethylmethylene(3-tert-butyl-5-methylcyclopentadienyl)fluorenylzirconium dichloride

#### (1) Synthesis of 1-tert-butyl-3-methylcyclopentadiene

25 [0243] To a solution obtained by adding 350 ml of dehydrated diethyl ether to 450 ml (0.90 mol) of a tert-butylmagnesium chloride/diethyl ether solution (concentration: 2.0 mol/liter), a solution of 43.7 g (0.45 mmol) of 3-methylcyclopentenone in 150 ml of dehydrated diethyl ether was dropwise added in a nitrogen atmosphere at 0°C with ice cooling, followed by stirring at room temperature for 15 hours. To the reaction solution, a solution of 80.0 g (1.50 mol) of ammonium chloride in 350 ml of water was dropwise added at 0°C with ice cooling. To the resulting solution, 2500  
30 ml of water was added, followed by stirring. Then, the organic phase was separated and washed with water. To the organic phase, 82 ml of a 10% hydrochloric acid aqueous solution was added at 0°C with ice cooling, followed by stirring at room temperature for 6 hours. The organic phase was separated from the reaction solution, washed with water, a saturated sodium hydrogencarbonate aqueous solution, water and a saturated saline solution, and then dried over anhydrous magnesium sulfate. The drying agent was filtered, and from the filtrate the solvent was distilled off to  
35 obtain a liquid. The liquid was subjected to vacuum distillation (45-47°C/10 mmHg) to obtain 14.6 g of a light yellow liquid. The analyzed values are given below.

[0244]  $^1\text{H}$ -NMR (270 MHz, in  $\text{CDCl}_3$ , based on TMS):  $\delta$ 6.31+6.13+5.94+5.87 (s+s+t+d, 2H), 3.04+2.95 (s+s, 2H), 2.17+2.09 (s+s, 3H), 1.27 (d, 9H)

#### 40 (2) Synthesis of 3-tert-butyl-1,6,6-trimethylfulvene

[0245] To a solution of 13.0 g (95.6 mmol) of 1-tert-butyl-3-methylcyclopentadiene in 130 ml of dehydrated methanol, 55.2 g (950.4 mmol) of dehydrated acetone was dropwise added in a nitrogen atmosphere at 0°C with ice cooling, and 68.0 g (956.1 mmol) of pyrrolidine was further dropwise added, followed by stirring at room temperature for 4 days.  
45 After the reaction solution was diluted with 400 ml of diethyl ether, 400 ml of water was added. The organic phase was separated, washed with a 0.5N hydrochloric acid aqueous solution (150 ml  $\times$  4), water (200 ml  $\times$  3) and a saturated saline solution (150 ml), and then dried over anhydrous magnesium sulfate. The drying agent was filtered, and from the filtrate the solvent was distilled off to obtain a liquid. The liquid was subjected to vacuum distillation (70-80°C/0.1 mmHg) to obtain 10.5 g of a yellow liquid. The analyzed values are given below.

50 [0246]  $^1\text{H}$ -NMP (270 MHz, in  $\text{CDCl}_3$ , based on TMS):  $\delta$ 6.23 (s, 1H), 6.05 (d, 1H), 2.23 (s, 3H), 2.17 (d, 6H), 1.17 (s, 9H)

#### (3) Synthesis of 2-(3-tert-butyl-5-methylcyclopentadienyl)-2-fluorenylpropane

55 [0247] To a solution of 10.1 g (60.8 mmol) of fluorene in 300 ml of THF, 40 ml (61.6 mmol) of a hexane solution of n-butyllithium was dropwise added in a nitrogen atmosphere with ice cooling, followed by stirring at room temperature for 5 hours (dark brown solution).

[0248] The solution was ice cooled again, and a solution of 11.7 g (66.5 mmol) of 3-tert-butyl-1,6,6-trimethylfulvene in 300 ml of THF was dropwise added in a nitrogen atmosphere. After stirring at room temperature for 14 hours, the

resulting brown solution was ice cooled, and 200 ml of water was added. The organic phase extracted with diethyl ether and separated was dried over magnesium sulfate and then filtered. From the filtrate, the solvent was removed under reduced pressure to obtain an orangy brown oil. The oil was purified by silica gel column chromatography (developing solvent: hexane) to obtain 3.8 g of a yellow oil. The analyzed values are given below.

[0249] <sup>1</sup>H-NMR (270 MHz, in CDCl<sub>3</sub>, Based on TMS): δ 7.70 (d, 4H), 7.34-7.26 (m, 6H), 7.18-7.11 (m, 6H), 6.17 (s, 1H), 6.01 (s, 1H), 4.42 (s, 1H), 4.27 (s, 1H), 3.01 (s, 2H), 2.87 (s, 2H), 2.17 (s, 3H), 1.99 (s, 3H), 2.10 (s, 9H), 1.99 (s, 9H), 1.10 (s, 6H), 1.07 (s, 6H)

#### (4) Synthesis of dimethylmethylene(3-tert-butyl-5-methylcyclopentadienyl)fluorenylzirconium dichloride

[0250] To a solution of 1.14 g (3.3 mmol) of 2-(3-tert-butyl-5-methylcyclopentadienyl)-2-fluorenylpropane in 25 ml of diethyl ether, 5.0 ml (7.7 mmol) of a hexane solution of n-butyllithium was dropwise added in a nitrogen atmosphere with ice cooling, and the mixture was stirred at room temperature for 14 hours to obtain a pink slurry. To the slurry, 0.77 g (3.3 mmol) of zirconium tetrachloride was added at -78°C, and the mixture was stirred at -78°C for several hours, followed by further stirring at room temperature for 65 hours. The resulting dark brown slurry was filtered. The substance remaining on the filter was washed with 10 ml of diethyl ether and extracted with dichloroethane to obtain a red solution. From the solution, the solvent was vacuum distilled off to obtain 0.53 g of a reddish orange solid. The analyzed values are given below.

<sup>1</sup>H-NMR (270 MHz, in CDCl<sub>3</sub>, Based on TMS): δ 8.11-8.02 (m, 3H), 7.82 (d, 1H), 7.56-7.45 (m, 2H), 7.23-7.17 (m, 2H), 6.08 (d, 1H), 5.72 (d, 1H), 2.59 (s, 3H), 2.41 (s, 3H), 2.30 (s, 3H), 1.08 (s, 9H)  
FD-MS: m/z = 500, 502, 504 (M<sup>+</sup>)

#### Example 2

#### Synthesis of cyclohexylidene(3-tert-butyl-5-methylcyclopentadienyl)fluorenylzirconium dichloride

##### (1) Synthesis of 3-tert-butyl-5-methyl-6,6-pentamethylenefulvene

[0251] To 50 ml of dehydrated methanol, 0.5 g (3.68 mmol) of 1-tert-butyl-3-methylcyclopentadiene and 3.81 ml (36.8 mmol) of cyclohexanone were added, then 3.07 ml (36.8 mmol) of pyrrolidine was dropwise added at 0°C, and the mixture was reacted at room temperature for 7 days. Then, 20 ml of water was added at 0°C. After extraction with ether, the organic phase was washed with water and successively dried over anhydrous magnesium sulfate. Then, the solvent was distilled off to obtain 1.3 g of a light yellow solid. The analyzed values are given below.

[0252] <sup>1</sup>H-NMR (270 MHz, in CDCl<sub>3</sub>, Based on TMS): δ 6.26 (s, 1H), 6.10 (s, 1H), 2.71 (dd, 2H), 2.61 (dd, 2H), 2.27 (d, 3H), 1.80-1.61 (m, 6H), 1.17 (s, 9H)

##### (2) Synthesis of 1-(3-tert-butyl-5-methylcyclopentadienyl)-1-fluorenylcyclohexane

[0253] To a solution of 0.8 g (4.5 mmol) of fluorene in 40 ml of THF, 2.9 ml (4.6 mmol) of a hexane solution of n-butyllithium was dropwise added in a nitrogen atmosphere with ice cooling, followed by stirring at room temperature for 6 hours. To the resulting red solution, a solution of 1.0 g (4.8 mmol) of 3-tert-butyl-5-methyl-6,6-pentamethylenefulvene in 15 ml of THF was dropwise added in a nitrogen atmosphere with ice cooling. After stirring at room temperature for 16 hours, 30 ml of water was added. The organic phase extracted with diethyl ether and separated was dried over magnesium sulfate and then filtered. From the filtrate, the solvent was removed under reduced pressure to obtain a light yellow liquid. The liquid was passed through a silica gel column using hexane as an eluent. From the resulting hexane solution, the solvent was removed under reduced pressure to obtain 1.3 g of a light yellow solid. The analyzed values are given below.

[0254] <sup>1</sup>H-NMR (270 MHz, in CDCl<sub>3</sub>, Based on TMS): δ 7.64 (d, 2H), 7.34-7.24 (m, 4H), 7.16-7.10 (m, 2H), 5.79 (s, 1H), 4.02 (s, 1H), 2.87-2.77 (s+s, 3H), 2.26-2.00 (m, 2H), 1.75-1.60 (s+s, 3H), 1.55-1.23 (m, 8H), 1.12 (d, 9H)

##### (3) Synthesis of cyclohexylidene(3-tert-butyl-5-methylcyclopentadienyl)fluorenylzirconium dichloride

[0255] To a solution of 1.3 g (3.3 mmol) of 1-(3-tert-butyl-5-methylcyclopentadienyl)-1-fluorenylcyclohexane in 40 ml of THF, 4.8 ml (6.8 mmol) of a hexane solution of n-butyllithium was dropwise added in a nitrogen atmosphere with ice cooling, followed by stirring at room temperature for 16 hours. From the reaction mixture, the solvent was removed under reduced pressure to obtain a reddish orange solid. To the solid, 150 ml of dichloromethane was added at -78°C, and they were stirred to give a solution. Then, the solution was added to 10 ml of a dichloromethane suspension of

1.1 g (2.9 mmol) of zirconium tetrachloride (THF) 2-complex having been cooled to -78°C, and the mixture was stirred at -78°C for 6 hours, followed by further stirring at room temperature for one day and night. From the reaction solution, the solvent was removed under reduced pressure to obtain a vermilion solid. The solid was extracted with diethyl ether and subjected to seltite filtration. The filtrate was concentrated to precipitate 18 mg of a reddish brown solid, and the solid was separated from the mother liquor. The analyzed values are given below.

<sup>1</sup>H-NMR (270 MHz, in CDCl<sub>3</sub>, Based on TMS): δ 8.10 (m, 2H), 7.90 (d, 1H), 7.76 (d, 1H), 7.56-7.46 (m, 2H), 7.28-7.18 (m, 2H), 6.07 (d, 1H), 5.72 (d, 1H), 3.73 (br, 1H), 3.34 (br, 1H), 2.55-2.33 (m, 2H), 2.27 (s, 3H), 2.05-1.64 (m, 6H), 1.08 (s, 9H)

FD-MS: m/z = 540, 542, 544 (M<sup>+</sup>)

#### Reference Example

##### Synthesis of 3,6-di-tert-butylfluorene

###### (1) Synthesis of 4,4'-di-t-butylidiphenylmethane

[0256] A 300 ml two-necked flask was thoroughly purged with nitrogen. In the flask, 38.4 g (289 mmol) of AlCl<sub>3</sub> was placed, and 80 ml of CH<sub>3</sub>NO<sub>2</sub> was added to give a solution (1). Separately, a 500 ml three-necked flask equipped with a dropping funnel and a magnetic stirrer was thoroughly purged with nitrogen. In the flask, 25.6 g (152 mmol) of diphenylmethane and 43.8 g (199 mmol) of 2,6-di-t-butyl-4-methylphenol were placed, and 80 ml of CH<sub>3</sub>NO<sub>2</sub> was added to give a solution. With stirring, this solution was cooled with an ice bath. To the solution was dropwise added the solution (1) over a period of 35 minutes, and the reaction solution was stirred at 12°C for 1 hour. The reaction solution was poured into 500 ml of ice water and extracted with 800 ml of hexane. The organic phase was washed with 600 ml of a 5% NaOH aqueous solution and dried over MgSO<sub>4</sub>. Then, the MgSO<sub>4</sub> was filtered off, and the solvent was evaporated to obtain an oil. The oil was cooled to -78°C to precipitate a solid. The solid was recovered by filtration, washed with 300 ml of EtOH and dried under reduced pressure to obtain 4,4'-di-t-butylidiphenylmethane (yield: 18.9 g).

###### (2) Synthesis of 2,2'-diiodo-4,4'-di-t-butylidiphenylmethane

[0257] In a 200 ml flask equipped with a magnetic stirrer, 1.95 g (6.96 mmol) of 4,4'-di-t-butylidiphenylmethane, 0.78 g (3.48 mmol) of HIO<sub>4</sub>, 1.55 g (6.12 mmol) of I<sub>2</sub> and 0.48 ml of concentrated H<sub>2</sub>SO<sub>4</sub> were placed. Then, 17.5 ml of acetic acid and 3.75 ml of water were added, and the mixture was heated to 90°C with stirring and reacted for 5 hours. The reaction solution was poured into 50 ml of ice water and extracted with Et<sub>2</sub>O. The organic phase was washed with 100 ml of a saturated NaHSO<sub>4</sub> aqueous solution, and then Na<sub>2</sub>CO<sub>3</sub> was added. After stirring, the Na<sub>2</sub>CO<sub>3</sub> was filtered off. The organic phase was washed with 800 ml of water, and Mg<sub>2</sub>SO<sub>4</sub> was added to dry the organic phase. After the Mg<sub>2</sub>SO<sub>4</sub> was filtered off, the solvent was distilled off to obtain a yellow oil. The oil was purified by column chromatography to obtain 2,2'-diiodo-4,4'-di-t-butylidiphenylmethane (yield: 3.21 g).

###### (3) Synthesis of 3,6-di-t-butylfluorene

[0258] In a 50 ml two-necked flask, 3.21 g (6.03 mmol) of 2,2'-diiodo-4,4'-di-t-butylidiphenylmethane was placed, and 2.89 g (47.0 mmol) of a copper powder was added. The mixture was heated to 230°C and reacted for 5 hours with stirring. After extraction with acetone, the solvent was distilled off to obtain a reddish brown oil. The oil was subjected to column chromatography to obtain a light yellow oil. The fractions containing the unreacted material was subjected to column chromatography again to recover the desired product only. The obtained product was recrystallized from methanol to obtain a white solid (yield: 1.08 g).

#### Example 3

##### Synthesis of dimethylmethylene(3-tert-butyl-5-methylcyclopentadienyl) (3,6-di-tert-butylfluorenyl)zirconium dichloride

###### (1) Synthesis of 2-(3-tert-butyl-5-methylcyclopentadienyl)-2-(3,6-di-tert-butylfluorenyl)propane

[0259] To a solution of 0.9 g (3.4 mmol) of 3,6-di-tert-butylfluorene in 30 ml of THF, 2.1 ml (3.4 mmol) of a hexane solution of n-butyllithium was dropwise added in a nitrogen atmosphere with ice cooling, followed by stirring at room temperature for 6 hours. To the resulting red solution, a solution of 0.6 g (3.5 mmol) of 3-tert-butyl-5,6,6-trimethylfulvene in 15 ml of THF was dropwise added in a nitrogen atmosphere with ice cooling, followed by stirring at room temperature

for 12 hours. Then, 30 ml of water was added. The organic phase extracted with diethyl ether and separated was dried over magnesium sulfate and then filtered. From the filtrate, the solvent was removed under reduced pressure to obtain a solid. The solid was recrystallized from hot methanol to obtain 1.2 g of a light yellow solid. The analyzed values are given below.

[0260] <sup>1</sup>H-NMR (270 MHz, in CDCl<sub>3</sub>, Based on TMS) : δ 7.72 (d, 2H), 7.18-7.05 (m, 4H), 6.18-5.99 (s+s, 1H), 4.32-4.18 (s+s, 1H), 3.00-2.90 (s+s, 2H), 2.13-1.98 (t+s, 3H), 1.38 (s, 18H), 1.19 (s, 9H), 1.10 (d, 6H)

(2) Synthesis of dimethylmethylene(3-tert-butyl-5-methylcyclopentadienyl)(3,6-di-tert-butylfluorenyl)zirconium dichloride

[0261] To a solution of 1.3 g (2.8 mmol) of 2-(3-tert-butyl-5-methylcyclopentadienyl)-2-(3,6-di-tert-butylfluorenyl)propane in 40 ml of diethyl ether, 3.6 ml (5.8 mmol) of a hexane solution of n-butyllithium was dropwise added in a nitrogen atmosphere with ice cooling, followed by stirring at room temperature for 16 hours. From the reaction mixture, the solvent was removed under reduced pressure to obtain a reddish orange solid. To the solid, 150 ml of dichloromethane was added at -78°C, and they were stirred to give a solution. Then, the solution was added to a suspension of 1.0 g (2.7 mmol) of zirconium tetrachloride (THF) 2-complex in 10 ml of dichloromethane having been cooled to -78°C, and the mixture was stirred at -78°C for 6 hours, followed by further stirring at room temperature for one day and night. From the reaction solution, the solvent was removed under reduced pressure to obtain an orange solid. The solid was extracted with toluene and subjected to sellaite filtration. From the filtrate, the solvent was removed under reduced pressure, and the residue was recrystallized from diethyl ether to obtain 0.18 g of an orange solid. The analyzed values are given below.

<sup>1</sup>H-NMR (270 MHz, in CDCl<sub>3</sub>, Based on TMS): δ 7.98 (dd, 2H), 7.90 (d, 1H), 7.69 (d, 1H), 7.32-7.25 (m, 2H), 6.01 (d, 1H), 5.66 (d, 1H), 2.54 (s, 3H), 2.36 (s, 3H), 2.28 (s, 1H), 1.43 (d, 18H), 1.08 (s, 9H)

FD-MS: m/z = 612, 614, 616 (M<sup>+</sup>)

#### Example 4

Synthesis of cyclohexylidene(3-tert-butyl-5-methylcyclopentadienyl)(3,6-di-tert-butylfluorenyl)zirconium dichloride

(1) Synthesis of 1-(3-tert-butyl-5-methylcyclopentadienyl)-1-(3,6-di-tert-butylfluorenyl)cyclohexane

[0262] To a solution of 0.81 g (2.91 mmol) of 3,6-di-tert-butylfluorene in 40 ml of THF, 1.91 ml (3.06 mmol) of a hexane solution of n-butyllithium was dropwise added in a nitrogen atmosphere at 0°C, followed by stirring at room temperature for 16 hours. To the resulting solution, a solution of 0.69 g (3.20 mmol) of 3-tert-butyl-5-methyl-6,6-pentamethylene-fulvene in 30 ml of THF was dropwise added in a nitrogen atmosphere at 0°C, followed by stirring at room temperature for 16 hours, to perform reaction. After the reaction, 30 ml of water was added. The organic phase was extracted with ether and dried over anhydrous magnesium sulfate. From the resulting solution, the solvent was distilled off under reduced pressure to obtain 1.26 g of a yellow solid. The analyzed values are given below.

[0263] <sup>1</sup>H-NMR (270 MHz, in CDCl<sub>3</sub>, Based on TMS): δ 7.64 (d, 2H), 7.22 (d, 2H), 7.15 (d,d, 2H), 6.10, 5.76 (1H), 3.89 (s, 1H), 2.82-2.58 (2H), 1.70 (s, 3H), 1.38 (s, 18H), 1.09 (s, 9H), 2.26-1.25 (10H)

(2) Synthesis of cyclohexylidene(3-tert-butyl-5-methylcyclopentadienyl)(3,6-di-tert-butylfluorenyl)zirconium dichloride

[0264] To a solution of 1.22 g (2.47 mmol) of 1-(3-tert-butyl-5-methylcyclopentadienyl)-1-(3,6-di-tert-butylfluorenyl)cyclohexane in 50 ml of THF, 3.39 ml (5.43 mmol) of a hexane solution of n-butyllithium was dropwise added in a nitrogen atmosphere with ice cooling, followed by stirring at room temperature for 16 hours. From the reaction mixture, the solvent was removed under reduced pressure to obtain a reddish orange solid. To the solid, a solution of 0.93 g (2.47 mmol) of zirconium tetrachloride (THF) 2-complex in 100 ml of dichloromethane having been cooled to -78°C was added. The mixture was stirred and reacted while the temperature of the mixture was allowed to naturally rise to room temperature. The resulting red suspension was subjected to sellaite filtration to remove lithium chloride. Then, to the orange filtrate was added 10 ml of toluene, and the mixture was concentrated until a solid was precipitated, followed by cooling to -20°C. The precipitated solid was recovered and then recrystallized from toluene to obtain 27 mg of a red solid. The analyzed values are given below.

<sup>1</sup>H-NMR (270 MHz, in CDCl<sub>3</sub>, Based on TMS): δ 8.02 (d, 1H), 7.97 (d, 1H), 7.76 (d, 1H), 7.62 (d, 1H), 7.33-7.29 (d,d, 2H), 6.01 (d, 1H), 5.66 (d, 1H), 3.69 (br,d, 1H), 3.29 (br,d, 1H), 2.25 (s, 3H), 2.54-1.53 (m, 8H), 1.44 (s, 9H), 1.43 (s, 9H), 1.07 (s, 9H)

Comparative Example 3Properties of random PP prepared using Ziegler-Natta catalyst

[0413] Properties of commercially available random PP (trade name: F637, available from Grand Polymer Co.) obtained by the use of a magnesium chloride-supported titanium catalyst are as follows. This polymer had T<sub>m</sub> of 142°C, MFR of 6 g/10 min, Mw/Mn of 6.0 and a decane-soluble component quantity of 8.0 % by weight, and the value of Mw/Mn was large. As the stereoregularity of the polymer, the mmmm was 91.1 %, and none of the 2,1-Insertion and the 1,3-insertion were detected.

Comparative Example 4Properties of thermally decomposed product of random PP prepared using Ziegler-Natta catalyst

[0414] Commercially available random PP (trade name: F637, available from Grand Polymer Co.) obtained by the use of a magnesium chloride-supported titanium catalyst was thermally decomposed under the conditions of 400°C and 100 minutes. Properties of the thus thermally decomposed polymer are as follows. This polymer had T<sub>m</sub> of 140°C, MFR of 1000 g/10 min, Mw/Mn of 2.3 and a decane-soluble component quantity of 22 % by weight, and the decane-soluble component quantity was large. As the stereoregularity of the polymer, the mmmm was 92.0 %, and none of the 2,1-insertion and the 1,3-insertion were detected.

~~Example 47~~Normal pressure polymerization of propylene using dimethylmethylene(3-tert-butyl-5-methylcyclopentadienyl)(2,7-di-tert-butylfluorenyl)zirconium dichloride

[0415] A 500 ml glass polymerization apparatus thoroughly purged with nitrogen was charged with 250 ml of dry toluene, and then propylene was bubbled to saturate the apparatus. Thereafter, a catalyst solution obtained by adding 5 mmol (in terms of aluminum) of methylaluminoxane (available from Albemarle Co.) to a toluene solution of 2.35 mg (3.8 μmol) of the red solid obtained in Example 5 was added. With stirring, polymerization was conducted at 25°C for 60 minutes while propylene was bubbled. Thereafter, methanol and a small amount of hydrochloric acid were added to terminate the polymerization. The resulting polymer was filtered, washed with methanol and dried under vacuum at 80°C for 6 hours. The quantity of the polymer obtained was 0.50 g. This polymer had T<sub>m</sub> of 140°C.

~~Example 48~~Normal pressure polymerization of propylene using dimethylmethylene(3-tert-butyl-5-methylcyclopentadienyl)(2,7-di-tert-butylfluorenyl)zirconium dichloride

[0416] Polymerization was carried out in the same manner as in Example 47, except that 10.3 mg (16.75 μmol) of the red solid obtained in Example 5 was used, and the polymerization temperature was changed to 50°C. The quantity of the polymer obtained was 6.2 g. This polymer had T<sub>m</sub> of 138°C.

Example 49Normal pressure polymerization of propylene using cyclohexylidene(3-tert-butyl-5-methylcyclopentadienyl)(3,6-di-tert-butylfluorenyl)zirconium dichloride

[0417] A 500 ml glass polymerization apparatus thoroughly purged with nitrogen was charged with 250 ml of dry toluene, and then propylene was bubbled to saturate the apparatus. Thereafter, a catalyst solution obtained by adding 5 mmol (in terms of aluminum) of methylaluminoxane (available from Albemarle Co.) to a toluene solution of 3.27 mg (5.0 μmol) of the red solid obtained in Example 4 was added. With stirring, polymerization was conducted at 25°C for 30 minutes while propylene was bubbled. Thereafter, methanol and a small amount of hydrochloric acid were added to terminate the polymerization. The resulting polymer was filtered, washed with methanol and dried under vacuum at 80°C for 6 hours. The quantity of the polymer obtained was 0.9 g. This polymer had T<sub>m</sub> of 155°C.

Example 50

Normal pressure polymerization of propylene using cyclohexylidene(3-tert-butyl-5-methylcyclopentadienyl)(3,6-di-tert-butylfluorenyl)zirconium dichloride

[0418] Polymerization was carried out in the same manner as in Example 49, except that the polymerization temperature was changed to 50°C. The quantity of the polymer obtained was 4.9 g. This polymer had T<sub>m</sub> of 144°C.

Example 51

Normal pressure polymerization of propylene using cyclohexylidene(3-tert-butyl-5-methylcyclopentadienyl)fluorenylzirconium dichloride

[0419] A 500 ml glass polymerization apparatus thoroughly purged with nitrogen was charged with 250 ml of dry toluene, and then propylene was bubbled to saturate the apparatus. Thereafter, a catalyst solution obtained by adding 5 mmol (in terms of aluminum) of methylaluminoxane (available from Albemarle Co.) to a toluene solution of 2.71 mg (5.0 μmol) of the reddish brown solid obtained in Example 2 was added. With stirring, polymerization was conducted at 25°C for 15 minutes while propylene was bubbled. Thereafter, methanol and a small amount of hydrochloric acid were added to terminate the polymerization. The resulting polymer was filtered, washed with methanol and dried under vacuum at 80°C for 6 hours. The quantity of the polymer obtained was 1.3 g. This polymer had T<sub>m</sub> of 145°C.

Example 52

Normal pressure polymerization of propylene using cyclohexylidene(3-tert-butyl-5-methylcyclopentadienyl)fluorenylzirconium dichloride

[0420] Polymerization was carried out in the same manner as in Example 51, except that the polymerization temperature was changed to 50°C. The quantity of the polymer obtained was 3.8 g. This polymer had T<sub>m</sub> of 139°C.

Example 53

Normal pressure polymerization of propylene using dimethylmethylene(3-(1-methyl-1-cyclohexyl)cyclopentadienyl)(3,6-di-tert-butylfluorenyl) zirconium dichloride

[0421] Polymerization of propylene was carried out in the same manner as in Example 47, except that 9.61 mg (5 μmol) of the orange solid obtained in Example 7 was used. The quantity of the polymer obtained was 0.3 g. This polymer had T<sub>m</sub> of 147°C.

Example 54

Normal pressure polymerization of propylene using dimethylmethylene(3-(1-methyl-1-cyclohexyl)cyclopentadienyl)(3,6-di-tert-butylfluorenyl)zirconium dichloride

[0422] Polymerization was carried out in the same manner as in Example 53, except that the polymerization temperature was changed to 50°C. The quantity of the polymer obtained was 0.2 g. This polymer had T<sub>m</sub> of 134°C.

Example 55

Normal pressure polymerization of propylene using dimethylmethylene(3-tert-butylcyclopentadienyl)(1,1,4,4,7,7,10,10-octamethyl-1,2,3,4,7,8,9,10-octahydrodibenzo(b,h)-fluorenyl)zirconium dichloride

[0423] Polymerization of propylene was carried out in the same manner as in Example 47, except that 1.7 mg (2.5 μmol) of the orange solid obtained in Example 8 was used. The quantity of the polymer obtained was 0.3 g. This polymer had T<sub>m</sub> of 143°C.

Example 56

Normal pressure polymerization of propylene using dimethylmethylene(3-tert-butylcyclopentadienyl)  
(1,1,4,4,7,7,10,10-octamethyl-1,2,3,4,7,8,9,10-octahydrodibenzo(b,h)-fluorenyl)zirconium dichloride

[0424] Polymerization was carried out in the same manner as in Example 55, except that the polymerization temperature was changed to 50°C. The quantity of the polymer obtained was 0.4 g. This polymer had T<sub>m</sub> of 140°C.

Example 57

Normal pressure polymerization of propylene using dimethylmethylene(3-trimethylsilylcyclopentadienyl)  
(1,1,4,4,7,7,10,10-octamethyl-1,2,3,4,7,8,9,10-octahydrodibenzo(b,h)-fluorenyl)zirconium dichloride

[0425] Polymerization of propylene was carried out in the same manner as in Example 47, except that 3.7 mg (5 μmol) of the red plate solid obtained in Example 9 was used. The quantity of the polymer obtained was 0.5 g. This polymer had T<sub>m</sub> of 137°C.

Example 58

Normal pressure polymerization of propylene using dimethylmethylene(3-trimethylsilylcyclopentadienyl)  
(1,1,4,4,7,7,10,10-octamethyl-1,2,3,4,7,8,9,10-octahydrodibenzo(b,h)-fluorenyl)zirconium dichloride

[0426] Polymerization was carried out in the same manner as in Example 57, except that the polymerization temperature was changed to 50°C. The quantity of the polymer obtained was 1.1 g. This polymer had T<sub>m</sub> of 142°C.

Example 59

Normal pressure polymerization of propylene using dimethylmethylene(3-(1,1-dimethylpropyl)cyclopentadienyl)  
(3,6-di-tert-butylfluorenyl)zirconium dichloride

[0427] Polymerization of propylene was carried out in the same manner as in Example 47, except that 3.07 mg (5 μmol) of the red solid obtained in Example 10 was used, and the polymerization time was changed to 45 minutes. The quantity of the polymer obtained was 1.1 g. This polymer had T<sub>m</sub> of 150°C.

Example 60

Normal pressure polymerization of propylene using dimethylmethylene(3-(1,1-dimethylpropyl)cyclopentadienyl)  
(3,6-di-tert-butylfluorenyl)zirconium dichloride

[0428] Polymerization was carried out in the same manner as in Example 59, except that the polymerization temperature was changed to 50°C. The quantity of the polymer obtained was 0.74 g. This polymer had T<sub>m</sub> of 138°C.

Example 61

Normal pressure polymerization of propylene using dimethylmethylene(3-(1-ethyl-1-methylpropyl)cyclopentadienyl)  
(3,6-di-tert-butylfluorenyl)-zirconium dichloride

[0429] Polymerization of propylene was carried out in the same manner as in Example 47, except that 3.15 mg (5 μmol) of the orange solid obtained in Example 11 was used. The quantity of the polymer obtained was 0.13 g. This polymer had T<sub>m</sub> of 142°C.

Example 62

Normal pressure polymerization of propylene using dimethylmethylene(3-(1-ethyl-1-methylpropyl)cyclopentadienyl)  
(3,6-di-tert-butylfluorenyl)zirconium dichloride

[0430] Polymerization was carried out in the same manner as in Example 61, except that the polymerization temperature was changed to 50°C. The quantity of the polymer obtained was 0.02 g. This polymer had T<sub>m</sub> of 123°C.

Example 63

Normal pressure polymerization of propylene using dimethylmethylene(3-(1,1,3-trimethylbutyl)cyclopentadienyl)(3,6-di-tert-butylfluorenyl)zirconium dichloride

[0431] Polymerization of propylene was carried out in the same manner as in Example 47, except that 3.22 mg (5  $\mu$ mol) of the reddish brown solid obtained in Example 12 was used. The quantity of the polymer obtained was 0.62 g. This polymer had Tm of 146°C.

Example 64

Normal pressure polymerization of propylene using dimethylmethylene(3-(1,1,3-trimethylbutyl)cyclopentadienyl)(3,6-di-tert-butylfluorenyl)zirconium dichloride

[0432] Polymerization was carried out in the same manner as in Example 63, except that the polymerization temperature was changed to 50°C. The quantity of the polymer obtained was 1.2 g. This polymer had Tm of 136°C.

Example 65

Normal pressure polymerization of propylene using dimethylmethylene(3-(1,1-dimethylbutyl)cyclopentadienyl)(3,6-di-tert-butylfluorenyl)zirconium dichloride

[0433] Polymerization of propylene was carried out in the same manner as in Example 47, except that 3.14 mg (5  $\mu$ mol) of the red solid obtained in Example 14 was used. The quantity of the polymer obtained was 1.67 g. This polymer had Tm of 149°C.

Example 66

Normal pressure polymerization of propylene using dimethylmethylene(3-(1,1-dimethylbutyl)cyclopentadienyl)(3,6-di-tert-butylfluorenyl)zirconium dichloride

[0434] Polymerization was carried out in the same manner as in Example 65, except that the polymerization temperature was changed to 50°C. The quantity of the polymer obtained was 1.2 g. This polymer had Tm of 137°C.

Example 67

Normal pressure polymerization of propylene using dimethylmethylene(3-tert-butylcyclopentadienyl)(2,7-di-tert-butylfluorenyl)zirconium dichloride

[0435] Polymerization of propylene was carried out in the same manner as in Example 47, except that 3.0 mg (5  $\mu$ mol) of the red solid obtained in Example 15 was used. The quantity of the polymer obtained was 1.27 g. This polymer had Tm of 140°C.

Example 68

Normal pressure polymerization of propylene using dimethylmethylene(3-tert-butylcyclopentadienyl)(2,7-di-tert-butylfluorenyl)zirconium dichloride

[0436] Polymerization was carried out in the same manner as in Example 67, except that the polymerization temperature was changed to 50°C. The quantity of the polymer obtained was 5.11 g. This polymer had Tm of 137°C.

Example 69

Normal pressure polymerization of propylene using diphenylmethylene(3-phenylcyclopentadienyl)(1,1,4,4,7,7,10,10-octamethyl-1,2,3,4,7,8,9,10-octahydrodibenzo(b,h)-fluorenyl)zirconium dichloride

[0437] Polymerization of propylene was carried out in the same manner as in Example 47, except that 4.27 mg (5  $\mu$ mol) of the reddish orange solid obtained in Example 17 was used. The quantity of the polymer obtained was 0.08



g. This polymer had T<sub>m</sub> of 105°C.

#### Example 70

Normal pressure polymerization of propylene using diphenylmethylen(3-trimethylsilylcyclopentadienyl) (1,1,4,4,7,7,10,10-octamethyl-1,2,3,4,7,8,9,10-octahydrodibenzo(b,h)fluorenyl)zirconium dichloride

[0438] Polymerization of propylene was carried out in the same manner as in Example 47, except that 4.05 mg (5 μmol) of the pink powder obtained in Example 18 was used. The quantity of the polymer obtained was 0.18 g. This polymer had T<sub>m</sub> of 139°C.

#### Example 71

Normal pressure polymerization of propylene using diphenylmethylen(3-trimethylsilylcyclopentadienyl) (1,1,4,4,7,7,10,10-octamethyl-1,2,3,4,7,8,9,10-octahydrodibenzo(b,h)fluorenyl)zirconium dichloride

[0439] Polymerization was carried out in the same manner as in Example 70, except that the polymerization temperature was changed to 50°C. The quantity of the polymer obtained was 0.64 g. This polymer had T<sub>m</sub> of 139°C.

#### Example 72

Normal pressure polymerization of propylene using methylphenylmethylen(3-tert-butylcyclopentadienyl) (3,6-di-tert-butylfluorenyl)zirconium dichloride

[0440] Polymerization of propylene was carried out in the same manner as in Example 47, except that 3.32 mg (5 μmol) of the orange solid obtained in Example 19 was used, and the polymerization time was changed to 45 minutes. The quantity of the polymer obtained was 1.16 g. This polymer had T<sub>m</sub> of 144°C.

#### Example 73

Normal pressure polymerization of propylene using methylphenylmethylen(3-tert-butylcyclopentadienyl) (3,6-di-tert-butylfluorenyl)zirconium dichloride

[0441] Polymerization was carried out in the same manner as in Example 72, except that the polymerization temperature was changed to 50°C. The quantity of the polymer obtained was 8.65 g. This polymer had T<sub>m</sub> of 144°C.

#### Example 74

Normal pressure polymerization of propylene using diethylmethylen(3-tert-butylcyclopentadienyl) (3,6-di-tert-butylfluorenyl)zirconium dichloride

[0442] Polymerization of propylene was carried out in the same manner as in Example 47, except that 3.14 mg (5 μmol) of the orange solid obtained in Example 20 was used. The quantity of the polymer obtained was 0.83 g. This polymer had T<sub>m</sub> of 150°C.

#### Example 75

Normal pressure polymerization of propylene using diethylmethylen(3-tert-butylcyclopentadienyl) (3,6-di-tert-butylfluorenyl)zirconium dichloride

[0443] Polymerization was carried out in the same manner as in Example 74, except that the polymerization temperature was changed to 50°C. The quantity of the polymer obtained was 3.15 g. This polymer had T<sub>m</sub> of 143°C.

Example 76

Normal pressure polymerization of propylene using cyclohexylidene(3-trimethylsilylcyclopentadienyl)(3,6-di-tert-butylfluorenyl)zirconium dichloride

[0444] Polymerization of propylene was carried out in the same manner as in Example 47, except that 3.3 mg (5  $\mu$ mol) of the orange solid obtained in Example 21 was used. The quantity of the polymer obtained was 0.58 g.

[0445] This polymer had Tm of 141°C.

Example 77

Normal pressure polymerization of propylene using cyclohexylidene(3-trimethylsilylcyclopentadienyl)(3,6-di-tert-butylfluorenyl)zirconium dichloride

[0446] Polymerization was carried out in the same manner as in Example 76, except that the polymerization temperature was changed to 50°C. The quantity of the polymer obtained was 0.8 g. This polymer had Tm of 139°C.

Example 78

Normal pressure polymerization of propylene using cyclopentylidene(3-tert-butylcyclopentadienyl)(3,6-di-tert-butylfluorenyl)zirconium dichloride

[0447] Polymerization of propylene was carried out in the same manner as in Example 47, except that 3.13 mg (5  $\mu$ mol) of the orange solid obtained in Example 22 was used. The quantity of the polymer obtained was 0.3 g. This polymer had Tm of 146°C.

Example 79

Normal pressure polymerization of propylene using cyclopentylidene(3-tert-butylcyclopentadienyl)(3,6-di-tert-butylfluorenyl)zirconium dichloride

[0448] Polymerization was carried out in the same manner as in Example 78, except that the polymerization temperature was changed to 50°C. The quantity of the polymer obtained was 3.1 g. This polymer had Tm of 143°C.

Example 80

Normal pressure polymerization of propylene using cyclohexylidene(3-(1,1-dimethylpropyl)cyclopentadienyl)(3,6-di-tert-butylfluorenyl)zirconium dichloride

[0449] Polymerization of propylene was carried out in the same manner as in Example 47, except that 3.28 mg (5  $\mu$ mol) of the reddish brown solid obtained in Example 23 was used. The quantity of the polymer obtained was 0.37 g. This polymer had Tm of 143°C.

Example 81

Normal pressure polymerization of propylene using cyclohexylidene(3-(1,1-dimethylpropyl)cyclopentadienyl)(3,6-di-tert-butylfluorenyl)zirconium dichloride

[0450] Polymerization was carried out in the same manner as in Example 80, except that the polymerization temperature was changed to 50°C. The quantity of the polymer obtained was 0.19 g. This polymer had Tm of 129°C.

Example 82

Normal pressure polymerization of propylene using cyclopentylidene(3-tert-butylcyclopentadienyl)(1,1,4,4,7,7,10,10-octamethyl-1,2,3,4,7,8,9,10-octahydrodibenzo(b,h)-fluorenyl)zirconium dichloride

[0451] Polymerization of propylene was carried out in the same manner as in Example 47, except that 3.67 mg (5  $\mu$ mol) of the red solid obtained in Example 24 was used. The quantity of the polymer obtained was 0.33 g.

Example 83

Normal pressure polymerization of propylene using cyclopentylidene(3-tert-butylcyclopentadienyl)  
(1,1,4,4,7,7,10,10-octamethyl-1,2,3,4,7,8,9,10-octahydrodibenzo(b,h)fluorenyl)zirconium dichloride

[0452] Polymerization was carried out in the same manner as in Example 82, except that the polymerization temperature was changed to 50°C. The quantity of the polymer obtained was 0.37 g.

Example 84

Bulk polymerization of propylene using cyclohexylidene(3-tert-butyl-5-methylcyclopentadienyl)fluorenylzirconium dichloride

[0453] In a 50 ml two-necked flask thoroughly purged with nitrogen, 2.0 mmol (in terms of aluminum) of silica-supported methylaluminoxane was suspended in 20 ml of heptane. To the suspension, a toluene solution of 1.1 mg (2 μmol) of the reddish brown solid obtained in Example 2 was added, then triisobutylaluminum (1 mmol) was added, and they were stirred for 30 minutes to give a catalyst suspension.

[0454] A 2000 ml autoclave thoroughly purged with nitrogen was charged with 500 g of propylene, and the catalyst suspension was added to perform polymerization at 70°C for 40 minutes under a pressure of 3.0 to 3.5 MPa. Thereafter, methanol was added to terminate the polymerization, and propylene was purged of, to obtain a polymer. The polymer was dried under vacuum at 80°C for 6 hours. The quantity of the polymer obtained was 103 g. This polymer had T<sub>m</sub> of 139°C, MFR of 1.2 g/10 min, Mw of 348000, Mn of 184000, Mw/Mn of 1.9 and a decane-soluble component quantity of 0.5 % by weight.

Example 85

Bulk polymerization of propylene using cyclohexylidene(3-tert-butyl-5-methylcyclopentadienyl)fluorenylzirconium dichloride

[0455] Polymerization of propylene was carried out in the same manner as in Example 84, except that 2 NL of hydrogen was added. The quantity of the polymer obtained was 55 g. This polymer had T<sub>m</sub> of 141°C, MFR of 1000 g/10 min, Mw of 69000, Mn of 30000, Mw/Mn of 2.3 and a decane-soluble component quantity of 0.8 % by weight. As the stereoregularity of the polymer, the mmmm was 85.8 %, the proportion of 2,1-insertion was 0.08 %, and the proportion of 1,3-insertion was 0.02 %.

Example 86

Bulk polymerization of propylene using cyclohexylidene(3-tert-butyl-5-methylcyclopentadienyl) (3,6-di-tert-butylfluorenyl)zirconium dichloride

[0456] Polymerization of propylene was carried out in the same manner as in Example 84, except that 1.3 mg (2 μmol) of the red solid obtained in Example 4 was used. The quantity of the polymer obtained was 49 g. This polymer had T<sub>m</sub> of 155°C, MFR of 1.6 g/10 min, Mw of 357000, Mn of 193000, Mw/Mn of 1.8 and a decane-soluble component quantity of 0.3 % by weight.

Example 87

Bulk polymerization of propylene using cyclohexylidene(3-tert-butyl-5-methylcyclopentadienyl)(3,6-di-tert-butylfluorenyl)zirconium dichloride

[0457] Polymerization of propylene was carried out in the same manner as in Example 86, except that 1 NL of hydrogen was added. The quantity of the polymer obtained was 328 g. This polymer had T<sub>m</sub> of 156°C, MFR of 150 g/10 min, Mw of 117000, Mn of 52000, Mw/Mn of 2.3 and a decane-soluble component quantity of 0.1 % by weight. As the stereoregularity of the polymer, the mmmm was 95.6 %, and none of the 2,1-insertion and the 1,3-insertion were detected.

Example 88

Bulk polymerization of propylene using cyclohexylidene(3-tert-butyl-5-methylcyclopentadienyl)(3,6-di-tert-butylfluorenyl)zirconium dichloride

[0458] Polymerization of propylene was carried out in the same manner as in Example 86, except that 1 NL of hydrogen was added, and the polymerization temperature was changed to 60°C. The quantity of the polymer obtained was 252 g. This polymer had T<sub>m</sub> of 158°C, MFR of 210 g/10 min, Mw of 97000, Mn of 45000, Mw/Mn of 2.1 and a decane-soluble component quantity of 0.1 % by weight. As the stereoregularity of the polymer, the mmmm was 97.0 %, and none of the 2,1-insertion and the 1,3-insertion were detected.

Example 89

Bulk polymerization of propylene using cyclohexylidene(3-tert-butyl-5-methylcyclopentadienyl) (3,6-di-tert-butylfluorenyl)zirconium dichloride

[0459] Polymerization of propylene was carried out in the same manner as in Example 86, except that 0.5 NL of hydrogen was added, and triethylaluminum (1 mmol) was used instead of triisobutylaluminum (1 mmol). The quantity of the polymer obtained was 295 g. This polymer had T<sub>m</sub> of 157°C, MFR of 42 g/10 min, Mw of 147000, Mn of 71000, Mw/Mn of 2.1 and a decane-soluble component quantity of 0.1 % by weight.

Example 90

Bulk polymerization of propylene using dimethylmethylene(3-tert-butyl-5-methylcyclopentadienyl)(2,7-di-tert-butylfluorenyl)zirconium dichloride

[0460] Polymerization of propylene was carried out in the same manner as in Example 84, except that 1.2 mg (2 μmol) of the red solid obtained in Example 5 was used. The quantity of the polymer obtained was 41 g. This polymer had T<sub>m</sub> of 141°C, MFR of 0.05 g/10 min, Mw of 524000, Mn of 274000, Mw/Mn of 1.9 and a decane-soluble component quantity of 0.1 % by weight. As the stereoregularity of the polymer, the mmmm was 88.4 %, the proportion of 2,1-insertion was 0.04 %, and the proportion of 1,3-insertion was 0.07 %.

Example 91

Bulk polymerization of propylene using dimethylmethylene(3-(1-methyl-1-cyclohexyl)cyclopentadienyl) (3,6-di-tert-butylfluorenyl)zirconium dichloride

[0461] Polymerization of propylene was carried out in the same manner as in Example 84, except that 4.5 mg (7 μmol) of the orange solid obtained in Example 7 was used. The quantity of the polymer obtained was 33 g. This polymer had T<sub>m</sub> of 146°C, MFR of 60 g/10 min, Mw of 115000, Mn of 67000, Mw/Mn of 1.7 and a decane-soluble component quantity of 0.7 % by weight.

Example 92

Bulk polymerization of propylene using dimethylmethylene(3-(1-methyl-1-cyclohexyl)cyclopentadienyl)(3,6-di-tert-butylfluorenyl)zirconium dichloride

[0462] Polymerization of propylene was carried out in the same manner as in Example 91, except that 1 NL of hydrogen was added. The quantity of the polymer obtained was 24 g. This polymer had T<sub>m</sub> of 153°C, MFR of 400 g/10 min, Mw of 59000, Mn of 30000, Mw/Mn of 2.0 and a decane-soluble component quantity of 1.0 % by weight.

Example 93

Bulk polymerization of propylene using dimethylmethylene(3-tert-butylcyclopentadienyl)(1,1,4,4,7,7,10,10-octamethyl-1,2,3,4,7,8,9,10-octahydrodibenzo(b,h)fluorenyl)zirconium dichloride

[0463] Polymerization of propylene was carried out in the same manner as in Example 84, except that 1.0 mg (1.4 μmol) of the orange solid obtained in Example 8 was used. The quantity of the polymer obtained was 30 g. This polymer

had Tm of 149°C and MFR of 190 g/10 min.

#### Example 94

Bulk polymerization of propylene using dimethylmethylene(3-tert-butylcyclopentadienyl)(1,1,4,4,7,7,10,10-octamethyl-1,2,3,4,7,8,9,10-octahydrodibenzo(b,h)fluorenyl)zirconium dichloride

[0464] Polymerization of propylene was carried out in the same manner as in Example 93, except that 0.3 NL of hydrogen was added. The quantity of the polymer obtained was 183 g. This polymer had Tm of 153°C and MFR of 1000 g/10 min.

#### Example 95

Bulk polymerization of propylene using dimethylmethylene(3-trimethylsilylcyclopentadienyl)(1,1,4,4,7,7,10,10-octamethyl-1,2,3,4,7,8,9,10-octahydrodibenzo(b,h)fluorenyl)zirconium dichloride

[0465] Polymerization of propylene was carried out in the same manner as in Example 84, except that 10.68 mg (0.94 µmol) of the red plate solid obtained in Example 9 was used. The quantity of the polymer obtained was 4 g. This polymer had Tm of 136°C.

#### Example 96

Bulk polymerization of propylene using dimethylmethylene(3-trimethylsilylcyclopentadienyl)(1,1,4,4,7,7,10,10-octamethyl-1,2,3,4,7,8,9,10-octahydrodibenzo(b,h)fluorenyl)zirconium dichloride

[0466] Polymerization of propylene was carried out in the same manner as in Example 95, except that 0.3 NL of hydrogen was added. The quantity of the polymer obtained was 64 g. This polymer had Tm of 143°C.

#### Example 97

Bulk polymerization of propylene using dimethylmethylene(3-(1,1-dimethylpropyl)cyclopentadienyl)(3,6-di-tert-butylfluorenyl)zirconium dichloride

[0467] Polymerization of propylene was carried out in the same manner as in Example 84, except that 0.68 mg (1.1 µmol) of the red solid obtained in Example 10 was used. The quantity of the polymer obtained was 54 g. This polymer had Tm of 151°C.

#### Example 98

Bulk polymerization of propylene using dimethylmethylene(3-(1,1-dimethylpropyl)cyclopentadienyl)(3,6-di-tert-butylfluorenyl)zirconium dichloride

[0468] Polymerization of propylene was carried out in the same manner as in Example 97, except that 0.3 NL of hydrogen was added. The quantity of the polymer obtained was 91 g. This polymer had Tm of 151°C.

#### Example 99

Bulk polymerization of propylene using dimethylmethylene(3-(1-ethyl-1-methylpropyl)cyclopentadienyl)(3,6-di-tert-butylfluorenyl)zirconium dichloride

[0469] Polymerization of propylene was carried out in the same manner as in Example 84, except that 0.68 mg (1.1 µmol) of the red solid obtained in Example 11 was used. The quantity of the polymer obtained was 12 g. This polymer had Tm of 147°C.

Example 100Bulk polymerization of propylene using

dimethylmethylene(3-(1-ethyl-1-methylpropyl)cyclopentadienyl)(3,6-di-tert-butyl-fluorenyl)zirconium dichloride

[0470] Polymerization of propylene was carried out in the same manner as in Example 99, except that 0.3 NL of hydrogen was added. The quantity of the polymer obtained was 34 g. This polymer had T<sub>m</sub> of 152°C.

Example 101

Bulk polymerization of propylene using dimethylmethylene(3-(1,1-dimethylbutyl)cyclopentadienyl)(3,6-di-tert-butylfluorenyl)zirconium dichloride

[0471] Polymerization of propylene was carried out in the same manner as in Example 84, except that 0.68 mg (1.1 μmol) of the red solid obtained in Example 14 was used. The quantity of the polymer obtained was 29 g. This polymer had T<sub>m</sub> of 147°C and MFR of 350 g/10 min.

Example 102

Bulk polymerization of propylene using dimethylmethylene(3-(1,1-dimethylbutyl)cyclopentadienyl)(3,6-di-tert-butylfluorenyl)zirconium dichloride

[0472] Polymerization of propylene was carried out in the same manner as in Example 101, except that 0.3 NL of hydrogen was added. The quantity of the polymer obtained was 43 g. This polymer had T<sub>m</sub> of 150°C and MFR of 1000 g/10 min.

Example 103

Bulk polymerization of propylene using dimethylmethylene(3-tert-butylcyclopentadienyl) (2,7-di-tert-butylfluorenyl) zirconium dichloride

[0473] Polymerization of propylene was carried out in the same manner as in Example 84, except that 1.3 mg (2 μmol) of the red solid obtained in Example 15 was used. The quantity of the polymer obtained was 42 g. This polymer had T<sub>m</sub> of 137°C and MFR of 1000 g/10 min.

Example 104

Bulk polymerization of propylene using dimethylmethylene(3-tert-butylcyclopentadienyl)(2,7-di-tert-butylfluorenyl) zirconium dichloride

[0474] Polymerization of propylene was carried out in the same manner as in Example 103, except that 0.3 NL of hydrogen was added. The quantity of the polymer obtained was 84 g. This polymer had T<sub>m</sub> of 138°C and MFR of 1000 g/10 min.

Example 105

Bulk polymerization of propylene using diphenylmethylene(3-trimethylsilylcyclopentadienyl) (1,1,4,4,7,7,10,10-octamethyl-1,2,3,4,7,8,9,10-octahydrodibenzo(b,h)fluorenyl)zirconium dichloride

[0475] Polymerization of propylene was carried out in the same manner as in Example 84, except that 0.68 mg (0.8 μmol) of the pink powder obtained in Example 18 was used. The quantity of the polymer obtained was 6 g. This polymer had T<sub>m</sub> of 141°C.

Example 106

Bulk polymerization of propylene using diphenylmethylene(3-trimethylsilylcyclopentadienyl)  
(1,1,4,4,7,7,10,10-octamethyl-1,2,3,4,7,8,9,10-octahydrodibenzo(b,h)fluorenyl)zirconium dichloride

[0476] Polymerization of propylene was carried out in the same manner as in Example 105, except that 0.3 NL of hydrogen was added. The quantity of the polymer obtained was 49 g. This polymer had Tm of 146°C.

Example 107

Bulk polymerization of propylene using methylphenylmethylene(3-tert-butylcyclopentadienyl) (3,6-di-tert-butylfluorenyl)zirconium dichloride

[0477] Polymerization of propylene was carried out in the same manner as in Example 84, except that 0.68 mg (2  $\mu$ mol) of the orange solid obtained in Example 19 was used. The quantity of the polymer obtained was 87 g. This polymer had Tm of 144°C.

Example 108

Bulk polymerization of propylene using methylphenylmethylene(3-tert-butylcyclopentadienyl) (3,6-di-tert-butylfluorenyl)zirconium dichloride

[0478] Polymerization of propylene was carried out in the same manner as in Example 107, except that 0.3 NL of hydrogen was added. The quantity of the polymer obtained was 148 g. This polymer had Tm of 146°C.

Example 109

Bulk polymerization of propylene using diethylmethylene(3-tert-butylcyclopentadienyl)(3,6-di-tert-butylfluorenyl)zirconium dichloride

[0479] Polymerization of propylene was carried out in the same manner as in Example 84, except that 0.68 mg (1.1  $\mu$ mol) of the orange solid obtained in Example 20 was used. The quantity of the polymer obtained was 50 g. This polymer had Tm of 149°C.

Example 110

Bulk polymerization of propylene using diethylmethylene (3-tert-butylcyclopentadienyl) (3,6-di-tert-butylfluorenyl)zirconium dichloride

[0480] Polymerization of propylene was carried out in the same manner as in Example 109, except that 0.3 NL of hydrogen was added. The quantity of the polymer obtained was 89 g. This polymer had Tm of 152°C.

Example 111

Bulk polymerization of propylene using cyclohexylidene(3-trimethylsilylcyclopentadienyl) (3,6-di-tert-butylfluorenyl)zirconium dichloride

[0481] Polymerization of propylene was carried out in the same manner as in Example 84, except that 0.68 mg (1  $\mu$ mol) of the orange solid obtained in Example 21 was used. The quantity of the polymer obtained was 20 g. This polymer had Tm of 139°C.

Example 112

Bulk polymerization of propylene using cyclohexylidene(3-trimethylsilylcyclopentadienyl)(3,6-di-tert-butylfluorenyl)zirconium dichloride

[0482] Polymerization of propylene was carried out in the same manner as in Example 111, except that 0.3 NL of hydrogen was added. The quantity of the polymer obtained was 43 g. This polymer had Tm of 141°C, MFR of 1000 g/

10 min and a decane-soluble component quantity of 0.5 % by weight.

#### Example 113

5 Bulk polymerization of propylene using cyclopentylidene(3-tert-butylcyclopentadienyl)(3,6-di-tert-butylfluorenyl) zirconium dichloride

[0483] Polymerization of propylene was carried out in the same manner as in Example 84, except that 0.68 mg (1.1  $\mu$ mol) of the orange solid obtained in Example 17 was used. The quantity of the polymer obtained was 49 g. This  
10 polymer had Tm of 149°C and MFR of 190 g/10 min.

#### Example 114

15 Bulk polymerization of propylene using cyclopentylidene(3-tert-butylcyclopentadienyl) (3,6-di-tert-butylfluorenyl) zirconium dichloride

[0484] Polymerization of propylene was carried out in the same manner as in Example 113, except that 0.3 NL of hydrogen was added. The quantity of the polymer obtained was 118 g. This polymer had Tm of 151°C and MFR of  
20 1000 g/10 min.

#### Example 115

25 Bulk polymerization of propylene using cyclohexylidene(3-(1,1-dimethylpropyl)cyclopentadienyl)(3,6-di-tert-butylfluorenyl)zirconium dichloride

[0485] Polymerization of propylene was carried out in the same manner as in Example 84, except that 0.68 mg (1  $\mu$ mol) of the reddish brown solid obtained in Example 23 was used. The quantity of the polymer obtained was 3 g. This  
30 polymer had Tm of 141°C.

#### Example 116

Bulk polymerization of propylene using cyclohexylidene(3-(1,1-dimethylpropyl)cyclopentadienyl)(3,6-di-tert-butylfluorenyl)zirconium dichloride

35 [0486] Polymerization of propylene was carried out in the same manner as in Example 115, except that 0.3 NL of hydrogen was added. The quantity of the polymer obtained was 47 g. This polymer had Tm of 150°C.

#### Example 117

40 Bulk polymerization of propylene using cyclopentylidene(3-tert-butylcyclopentadienyl)(1,1,4,4,7,7,10,10-octamethyl-1,2,3,4,7,8,9,10-octahydrodibenzo(b,h)fluorenyl)zirconium dichloride

[0487] Polymerization of propylene was carried out in the same manner as in Example 84, except that 0.68 mg (0.9  $\mu$ mol) of the red solid obtained in Example 24 was used. The quantity of the polymer obtained was 3 g. This polymer  
45 had Tm of 143°C.

#### Example 118

50 Bulk polymerization of propylene using cyclopentylidene(3-tert-butylcyclopentadienyl) (1,1,4,4,7,7,10,10-octamethyl-1,2,3,4,7,8,9,10-octahydrodibenzo(b,h)fluorenyl)zirconium dichloride

[0488] Polymerization of propylene was carried out in the same manner as in Example 117, except that 0.3 NL of hydrogen was added. The quantity of the polymer obtained was 87 g. This polymer had Tm of 152°C.



Comparative Example 5Bulk polymerization of propylene using dimethylsilylenebis(2-methyl-4,5-benzoindenyl)zirconium dichloride

[0489] Polymerization of propylene was carried out in the same manner as in Example 84, except that 0.8 mg of dimethylsilylenebis(2-methyl-4,5-benzoindenyl)zirconium dichloride was used as metallocene. The quantity of the polymer obtained was 150 g. This polymer had T<sub>m</sub> of 145°C, MFR of 16 g/10 min, Mw/Mn of 2.1 and a decane-soluble component quantity of 0.4 % by weight. As the stereoregularity of the polymer, the mmmm was 93.0 %, the proportion of 2,1-insertion was 0.75 %, the proportion of 1,3-insertion was 0.06 %, and the proportion of the 2,1-insertion was high.

Comparative Example 6Bulk polymerization of propylene using dimethylsilylenebis(2-methyl-4-phenylindenyl)zirconium dichloride

[0490] Polymerization of propylene was carried out in the same manner as in Example 84, except that 0.7 mg of dimethylsilylenebis(2-methyl-4-phenylindenyl)zirconium dichloride was used as metallocene. The quantity of the polymer obtained was 163 g. This polymer had T<sub>m</sub> of 150°C, MFR of 1 g/10 min, Mw/Mn of 2.5 and a decane-soluble component quantity of 0.6 % by weight. As the stereoregularity of the polymer, the mmmm was 95.9 %, the proportion of 2,1-insertion was 0.80 %, the proportion of 1,3-insertion was 0.05 %, and the proportion of the 2,1-insertion was high.

Comparative Example 7Properties of homo-PP prepared using Ziegler-Natta catalyst

[0491] Properties of commercially available homo-PP (trade name: J700, available from Grand Polymer Co.) obtained by the use of a magnesium chloride-supported titanium catalyst are as follows. This polymer had T<sub>m</sub> of 161°C, MFR of 11 g/10 min, Mw/Mn of 5.2 and a decane-soluble component quantity of 2.0 % by weight, and the value of Mw/Mn was large. As the stereoregularity of the polymer, the mmmm was 95.0 %, and none of the 2,1-insertion and the 1,3-insertion were detected.

Comparative Example 8Properties of thermally decomposed product of homo-PP prepared using Ziegler-Natta catalyst

[0492] Commercially available homo-PP (trade name: J700, available from Grand Polymer Co.) obtained by the use of a magnesium chloride-supported titanium catalyst was thermally decomposed under the conditions of 400°C and 100 minutes. Properties of the thus thermally decomposed polymer are as follows. This polymer had T<sub>m</sub> of 160°C, MFR of 1000 g/10 min, Mw/Mn of 2.3 and a decane-soluble component quantity of 15 % by weight, and the decane-soluble component quantity was large. As the stereoregularity of the polymer, the mmmm was 94.9 %, and none of the 2,1-insertion and the 1,3-insertion were detected.

Example 119Normal pressure polymerization of propylene using dimethylmethylene(3-tert-butyl-5-methylcyclopentadienyl) (3,6-di-tert-butylfluorenyl)zirconium dichloride

[0493] A 500 ml glass polymerization apparatus thoroughly purged with nitrogen was charged with 250 ml of dry toluene, and then the apparatus was purged with propylene. Then, a catalyst solution obtained by adding 5 mmol (in terms of aluminum) of methylaluminumoxane (available from Albemarle Co.) to a toluene solution of 3.1 mg (5 μmol) of the orange solid obtained in Example 3 was added. With stirring, polymerization was conducted at 25°C for 30 minutes while propylene was bubbled. Thereafter, methanol and a small amount of hydrochloric acid were added to terminate the polymerization. The resulting polymer was filtered, washed with methanol and dried under vacuum at 80°C for 6 hours. The quantity of the polymer obtained was 0.7 g. This polymer had T<sub>m</sub> of 155°C.

Example 120

Normal pressure polymerization of propylene using dimethylmethylene(3-tert-butyl-5-methylcyclopentadienyl)(3,6-di-tert-butylfluorenyl)zirconium dichloride

[0494] Polymerization was carried out in the same manner as in Example 119, except that the polymerization temperature was changed to 50°C. The quantity of the polymer obtained was 1.6 g. This polymer had T<sub>m</sub> of 144°C.

Example 121

Normal pressure polymerization of propylene using dimethylmethylene(3-tert-butyl-5-methylcyclopentadienyl)fluorenylzirconium dichloride

[0495] A 500 ml glass polymerization apparatus thoroughly purged with nitrogen was charged with 250 ml of dry toluene, and then propylene was bubbled to saturate the apparatus. Thereafter, a catalyst solution obtained by adding 5 mmol (in terms of aluminum) of methylaluminoxane (available from Albemarle Co.) to a toluene solution of 2.51 mg (5.0 μmol) of the reddish orange solid obtained in Example 1 was added. With stirring, polymerization was conducted at 25°C for 10 minutes while propylene was bubbled. Thereafter, methanol and a small amount of hydrochloric acid were added to terminate the polymerization. The resulting polymer was filtered, washed with methanol and dried under vacuum at 80°C for 6 hours. The quantity of the polymer obtained was 0.9 g. This polymer had T<sub>m</sub> of 146°C.

Example 122

Normal pressure polymerization of propylene using dimethylmethylene(3-tert-butyl-5-methylcyclopentadienyl)fluorenylzirconium dichloride

[0496] Polymerization was carried out in the same manner as in Example 121, except that the polymerization temperature was changed to 50°C. The quantity of the polymer obtained was 0.9 g. This polymer had T<sub>m</sub> of 134°C.

Example 123

Bulk polymerization of propylene using dimethylmethylene(3-tert-butyl-5-methylcyclopentadienyl)fluorenylzirconium dichloride

[0497] In a 50 ml two-necked flask thoroughly purged with nitrogen, 2.0 mmol (in terms of aluminum) of silica-supported methylaluminoxane was suspended in 20 ml of heptane. To the suspension, a toluene solution of 1.0 mg (2 μmol) of the reddish orange solid obtained in Example 1 was added, then triisobutylaluminum (1 mmol) was added, and they were stirred for 30 minutes to give a catalyst suspension.

[0498] A 2000 ml autoclave thoroughly purged with nitrogen was charged with 500 g of propylene, and the catalyst suspension was added to perform polymerization at 70°C for 40 minutes under a pressure of 3.0 to 3.5 MPa. Thereafter, methanol was added to terminate the polymerization, and propylene was purged of, to obtain a polymer. The polymer was dried under vacuum at 80°C for 6 hours. The quantity of the polymer obtained was 102 g. This polymer had T<sub>m</sub> of 139°C, MFR of 0.7 g/10 min, Mw of 406000, Mn of 197000, Mw/Mn of 2.1 and a decane-soluble component quantity of 0.1 % by weight.

Example 124

Bulk polymerization of propylene using dimethylmethylene(3-tert-butyl-5-methylcyclopentadienyl)fluorenylzirconium dichloride

[0499] Polymerization of propylene was carried out in the same manner as in Example 123, except that 1 NL of hydrogen was added. The quantity of the polymer obtained was 69 g. This polymer had T<sub>m</sub> of 142°C, MFR of 22 g/10 min, Mw of 185000, Mn of 80000, Mw/Mn of 2.3 and a decane-soluble component quantity of 0.4 % by weight. As the stereoregularity of the polymer, the mmmm was 86.9 %, the proportion of 2,1-insertion was 0.02 %, and the proportion of 1,3-insertion was 0.05 %.

Example 125Bulk polymerization of propylene using dimethylmethylene(3-tert-butyl-5-methylcyclopentadienyl) (3,6-di-tert-butylfluorenyl)zirconium dichloride

[0500] Polymerization of propylene was carried out in the same manner as in Example 123, except that 1.1 mg (1.8  $\mu$ mol) of the orange solid obtained in Example 3 was used. The quantity of the polymer obtained was 90 g. This polymer had Tm of 154 °C, MFR of 1.8 g/10 min, Mw of 321000, Mn of 154000, Mw/Mn of 2.3 and a decane-soluble component quantity of 0.1 % by weight.

Example 126Bulk polymerization of propylene using dimethylmethylene(3-tert-butyl-5-methylcyclopentadienyl)(3,6-di-tert-butylfluorenyl)zirconium dichloride

[0501] Polymerization of propylene was carried out in the same manner as in Example 125, except that 1 NL of hydrogen was added. The quantity of the polymer obtained was 135 g. This polymer had Tm of 156°C, MFR of 350 g/10 min, Mw of 82000, Mn of 37000, Mw/Mn of 2.2 and a decane-soluble component quantity of 0.2 % by weight. As the stereoregularity of the polymer, the mmmm was 94.8 %, and none of the 2,1-insertion and the 1,3-insertion were detected.

Comparative Example 9Synthesis of dimethylmethylene (3-tert-butyl-5-methylcyclopentadienyl)fluorenylzirconium dichloride containing isomer

## (1) Synthesis of 2,6,6-trimethylfulvene

[0502] To 130 ml of dehydrated methanol, 22.6 g (283 mmol) of methylcyclopentadiene and 8.50 ml (116 mmol) of acetone were added, then 14.5 ml (174 mmol) of pyrrolidine was dropwise added at 0°C, and the mixture was reacted at room temperature for one night. Then, 10 ml (180 mmol) of acetic acid was added at 0°C. The mixture was diluted with ether and water and then subjected to extraction. Then, the organic phase was separated, washed with water and dried over anhydrous magnesium sulfate to obtain 12.9 g of a brown liquid. The analyzed values are given below.

[0503] <sup>1</sup>H-NMR (270 MHz, in CDCl<sub>3</sub>, Based on TMS, main peak):  $\delta$ 6.49 (d, 1H), 6.32 (d, 1H), 6.17 (s, 1H), 2.14 (s, 3H), 2.13 (s, 3H), 2.06 (s, 3H)

## (2) Synthesis of 1-tert-butyl-3-methylcyclopentadiene

[0504] In a 300 ml flask purged with nitrogen, 2.86 g (23.8 mmol) of trimethylfulvene synthesized in the above step (1) and 80 ml of dry ether were placed. Then, 17 ml (23.8 mmol) of a methyllithium/ether solution (concentration: 1.4 mol/liter) was dropwise added at -78°C, and the mixture was reacted at room temperature for 2 days. Then, 20 ml of an ammonium chloride saturated aqueous solution was added, and the organic phase was separated, washed with water, washed with a sodium chloride saturated aqueous solution and dried over anhydrous magnesium sulfate. Thereafter, the solvent was distilled off, and the residue was purified by column chromatography (silica gel, developing solvent: hexane) to obtain 2.04 g of a brown liquid. The analyzed values are given below.

[0505] <sup>1</sup>H-NMR (270 MHz, in CDCl<sub>3</sub>, Based on TMS, main peak):  $\delta$ 6.31+6.13+5.94+5.87 (s+s+t+d, 2H), 3.04+2.95 (s+s, 2H), 2.17+2.09 (s+s, 3H), 1.27 (d, 9H)

[0506] Peaks derived from proton of an isomer were observed in the vicinity of  $\delta$ 5.5 and 5.1. From the integral value of proton, the ratio of the presence between the main product and the by-product proved to be about 8:1.

## (3) Synthesis of dimethylmethylene(3-tert-butyl-5-methylcyclopentadienyl)fluorenylzirconium dichloride

[0507] Dimethylmethylene(3-tert-butyl-5-methylcyclopentadienyl)fluorenylzirconium dichloride was synthesized in the same manner as in the steps (3) and (4) of Example 1, except that 1-tert-butyl-3-methylcyclopentadiene containing an isomer obtained in the step (2) was used.

[0508] Peaks derived from proton of an isomer were observed in the vicinity of  $\delta$ 7.4 and 6.1. From the integral value of proton, the ratio of the presence between the main product and the by-product proved to be about 8:1.